THE PHOTODISSOCIATION OF BROMINE MOLECULES AND THE RECOMBINATION OF BROMINE ATOMS.

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CONTENTS.

EDINBURGH.

This is to certify that Mr WILLIAM SMITH, a candidate for the degree of Ph.D., successfully sustained an oral examination by a Committee of the Department on the subject of his thesis on 17 March, 1936.

Chairman of Committee.

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I N T R O D U C T I O N.

The study of the photochemistry of gases entered on a new phase with the work of Franck and Dymond on the fluorescence of iodine vapour in 1925. According to Franck (1) the primary process on the absorption of light by a molecule is excitation of the molecule. In the case of a homopolar molecule (e.g. halogen molecules) absorption of light of wavelength corresponding to the region of continuous absorption results in excitation followed immediately by dissociation without the intervention of a collision. Of the resulting atoms, one is in the normal state the other in the electronically excited state. At the convergence limit the atoms separate with negligibly small kinetic energies.

Franck's postulates were verified (2) experimentally by very thorough investigation of the band absorption spectra of chlorine, bromine and iodine. The spectra show a complicated system of absorption bands in the red and yellow parts of the spectrum. These bands converge to a limit from which continuous absorption extends towards the ultra-violet.

Turner/

Turner (2a) on the other hand made an exact determination of the energy levels of halogen atoms by a spectroscopic method. He was able to calculate how much of the light energy absorbed excites one of the atoms (from energy level (normal) 2^2P_1 to energy level (excited) 2^2P_2) resulting in dissociation. The values agreed very well with Franck's estimates. When they are taken into consideration along with the determined amount of energy corresponding to the convergence limit, a value for the heat of dissociation into two normal atoms is obtained which shows remarkable agreement with that obtained from thermo-chemical data. This may be seen from the following table.

MOLECULE	CONVERGENCE LIMIT. λ_c	$N h\nu$ (in Kg. Cal. for λ_c)	EXCITATION ENERGY OF THE ATOM. $2^2P_2 - 2^2P_1$	HEAT OF DISSOCIATION. (SPECTROSCOPIC)	HEAT OF DISSOCIATION (THERMOCHEM.)
Cl_2	4785Å	59.4	2.5 Kg. Cal	56.9 Kg. Cal.	57.0 Kcal
Br_2	5107	55.6	10.4	45.2	46.2
I_2	4995	56.8	21.6	35.2	34.5

That one of the atoms produced by photodissociation in the continuum is normal has also been shown by Turner (2b). When iodine vapour is illuminated by light/

light from a carbon arc, he found that the 1830.4 Å line of the iodine atom is more strongly absorbed than when the vapour is not illuminated. This indicates the presence of normal iodine atoms on the photodissociation of iodine.

Absorption in the region above the convergence limit may also result in dissociation. This takes place through the intermediary of a collision. If the excited molecule produced does not suffer a collision, the absorbed energy must be re-radiated as fluorescence. Dymond (3) has shown in the case of iodine vapour, that this can only take place in the region of discontinuous bands. He also showed that if the energy absorbed is sufficient to bring about dissociation there can be no re-radiation of absorbed energy as fluorescence.

Further evidence in favour of Franck's views has been obtained. By observing the change of resistance of a heated platinum wire place in bromine vapour on exposure to appropriate radiations, Senftleben and Germer (4) detected the dissociation of bromine molecules into bromine atoms. Dissociation into atoms causes the thermal conductivity of the gas to increase/

increase, the temperature of the wire falls and as a result there is a decrease in the resistance. By this method they were able to find the higher wavelength limit for the radiation necessary to produce dissociation. They examined chlorine and iodine in the same way. Their results show remarkable agreement with those obtained spectroscopically.

The photodissociation of halogen molecules has also been studied, qualitatively, by means of the Budde effect. Since this was the chief phenomenon examined in the present research it is desirable to give a short historical account of the work which has already been done.

The photoexpansion of chlorine and bromine was first observed by Budde (5). By interposing a water screen between the light source and the insolation vessel he showed that the expansion was independent of the direct heating effects of the light. He further observed that as long as the intensity of the light remains constant the volume to which the halogen vapour expands is maintained and that on shading contraction to the original volume takes place. Rays of high refrangibility, as Budde called them, were shown to produce the photoexpansion or Budde effect whereas/

whereas rays at the red end of the spectrum were ineffective.

Budde put forward three possible explanations of the phenomenon.

1. The expansion is due to an increased concentration of halogen atoms

$$\text{i.e. } Cl_2 = Cl + Cl$$

1 volume → 2 volumes.

2. Light performs some work which is converted into heat.

3. Chlorine is warmed up in the same way that lamp-black is warmed up in the heat spectrum.

However, this last possibility he rejected since the red end of the spectrum gave no photoexpansion. At first he was inclined to believe that 1. was the correct explanation, although he found later (6) that the expansion was accompanied by a rise in temperature.

It is interesting to note that in 1887, Bunsen and Roscoe (7) were of the belief that the expansion was brought about by the direct heating effects of the light.

Pringsheim (8) supported the work of Budde and showed the expansion to be different from the Draper effect. This effect observed by Draper during his experiments/

experiments on the hydrogen-chlorine combination, between 1841 and 1845, was that on illumination, the reaction $H_2 + Cl_2 = 2\ H\ Cl$ is followed by a marked increase of pressure. This has been interpreted as due to energy liberated in the reaction.

The Budde effect was further examined by Richardson (9). He took two bulbs, capacity 160 c.c., and joined them by means of a capillary containing some concentrated sulphuric acid. He filled the bulbs with air and immersed them in a tank through which a current of cold water circulated. Exposure to bright sunlight did not result in a movement of the sulphuric acid index. He now replaced air in one of the bulbs with dry chlorine and repeated the experiment. Exposure to sunlight resulted in a movement of the index through 20 - 30 cm. Shading brought the index back to the original position. Interposing blue glass had little effect whereas ruby glass caused the index to return to the zero position. Richardson believed that the effect was proportional to the light intensity.

In 1894 Baker (10) claimed that perfectly dry chlorine did not show photoexpansion. This claim has been supported and contradicted by various workers.

Shenstone (11) showed that the presence of a small/

small quantity of moist air in chlorine gave rise to an increased expansion on exposure to sunlight.

Mellor (12) in 1902 tried rather an ingenious experiment. He used concentric bulbs the outer one containing chlorine, the inner, air. On illumination he observed an expansion of the air as well as the chlorine. Thus he concluded that the photoexpansion is due to a temperature effect. (In this experiment the inner air bulb acted as a gas thermometer and indicated the rise in temperature of the walls.) He considered that the actinic energy continuously absorbed by moist chlorine is continuously dissipated in at least three ways, viz:-

1. partly in maintaining the chemical reaction

$$Cl_2 = Cl + Cl.$$

2. conversion into heat during molecular impacts,
3. partly as a re-radiation or fluorescence.

Mellor found no Budde effect in the case of dry chlorine.

Bevan (13) examined the effect by observing the change in resistance of a platinum wire suspended in the gas. He concluded that the expansion of moist chlorine was proportional to the rise in temperature.

As a result of some rough experiments Caldwell (14) considered that the rise in temperature was not sufficient/

sufficient to account for the expansion observed. To measure the temperature rise he used a Beckmann thermometer. He further showed that if the expansion was due to ionisation then the effect would be more noticeable in the case of chlorine than in bromine. Such was not the case, however.

Thereafter the problem gave rise to some controversy which still exists. Some maintained that the moist halogen alone showed the Budde effect. Others, said that it made no difference whether the halogen was moist or dry.

In 1924 Ludlam (15) decided dry bromine exhibited no Budde effect. On the basis of work by Perrin (16) he suggested that the energy absorbed was radiated again in all directions. He further concluded that when moisture is present it seems to facilitate dissociation into atoms, the energy of recombination giving rise to an increase in temperature of the gas.

Lewis and Rideal (17) maintained that since the presence of moisture seems necessary for the expansion, the effect is due to a photo-sensitive bromine hydrate of the composition Br_2, H_2O. They showed the photo-expansion to be proportional to both the partial pressure/

pressure of bromine and of water vapour. Further they found no photoexpansion with light of wavelength greater than $\lambda = 580 \mu\mu$.

Later (18) they advanced a mechanism of excitation and decomposition of bromine hydrate molecules as the explanation of the Budde effect.

Kistiakowsky (19) concluded that there was little doubt that drying reduced the photoexpansion of chlorine. He found that the absorption spectrum and the total absorption of light by chlorine was not appreciably affected by thorough drying. His belief was that water molecules have a catalytic effect on the rate of recombination of the atoms and therefore also on therate of dissociation of chlorine molecules.

On the other hand, Brown and Chapman (20) maintained that drying does not diminish the photo-expansion to any great extent with a mixture of air and bromine. This was contrary to the results obtained by Lewis and Rideal with air-bromine mixtures.

Matthews (21) said that although there was a diminution in the photoexpansion on drying bromine, it did not disappear entirely.

Ludlam and Mooney (22) did not agree in every respect/

respect with Matthews' results. They showed, since the latter had liquid bromine in contact with the vapour, that if the photoexpansion is due to a purely thermal effect it would not be possible to observe an expansion since the pressure would always remain the same no matter how the temperature in the bulbs varied. On the other hand they suggested that a small concentration of bromine atoms could produce a marked expansion. In the same paper they put forward an explanation of the effect of water. They further suggested that in the event of there being no adsorbed film of water on the surface of the containing vessel, then recombination of the halogen atoms would take place on the walls. The heat of recombination would be dissipated away the heat capacity of the walls being very much greater than that of the gas. They also found that the energy absorbed by bromine was not re-radiated as fluorescence at the pressure used (viz. 64 mm).

Shortly after this, Kistiakowsky (23) found that careful purification and drying of bromine and chlorine produced no change in the photoexpansion. He even went so far as to remove the adsorbed film of water from/

from the walls by "baking" out the containing vessel at 300°C. He found that this made little or no impression on the photoexpansion. Inside the vessel was placed an almost hair-fine capillary through which a platinum wire was drawn. The arrangement was such that only glass was in contact with the halogen vapour, the ends of the wire being carried to the outside of the vessel. He used the wire as a platinum resistance thermometer and showed that the temperature change agreed fairly well with the expansion on illumination.

Martin, Cole and Lent (24) using chlorine at atmospheric pressure concluded that careful purification and drying and the "baking" out of the insolation vessel have no appreciable effect on the photoexpansion.

On the other hand Narayana (25) showed that in pure super-dried chlorine there was no photoexpansion. He further showed that as the halogens, chlorine and bromine, were gradually dried a marked decrease in the photoexpansion can be observed. He also claimed that in the band absorption region photo-expansion was absent. (This latter claim does not seem/

seem reasonable. The pressures of vapour used (viz. 760 mm. chlorine and 250 mm. bromine) were high. Absorption of light above the convergence limit (convergence limit:- chlorine λ_c = 4780 Å, bromine λ_c = 5107Å) results in the production of activated molecules which will dissociate on collision. At the pressures Narayana used the number of collisions would be great. Thus a considerable number of activated molecules would be dissociated. The photoexpansion, however, resulting from the heat of recombination of the atoms may have been too small for him to recognise with his pressure gauge).

Narayana (26) also examined the Budde effect in iodine. This he did at two temperatures 200°C. and 350°C. He claimed that since the photoexpansion was greater in the former case, the effect of the walls was shown. This was supposed due to the fact that at 200° the adsorbed film of water is still present on the walls whereas at 350° it is completely absent, and the dry walls will catalyse recombination of the atoms. (Cf Wood (27) on recombination of hydrogen atoms on the surface of dry glass).

The above survey of the Budde effect from 1871 until/

until 1934 shows that there has been considerable variation of opinion as to the effect of moisture. Why there should be a decrease of the photoexpansion on the removal of water vapour has not been satisfactorily explained.

There are several other interesting points with regard to the effect of moisture which have resulted from an examination of the action of light on the halogens.

Several investigators (28) have failed to detect any difference between the absorption coefficients of moist chlorine and that which has been thoroughly dried.

Martin and Cole (29) examined the scattering of light by moist and dry chlorine. Both scattered normally i.e. the intensity of the scattered light agreed with that calculated from the Rayleigh formula, and was a thousandfold less than the hypothetical isochromatic fluorescence which would be required to explain say Shenstone's results.

In 1927 Kistiakowsky (19) found that extreme drying of chlorine did not alter appreciably the structure of the/

the absorption spectrum or the total amount of energy absorbed. He considered that less than 5% of the absorbed light energy was re-emitted as fluorescence by dried chlorine. He suggested that halogens dissociate into atoms on absorption of light energy in the region of continuous absorption independently of the purity.

Weigert and Nicolai (30) concluded from the similarity of the absorption of light by moist and dry chlorine that this was only reconcilable with Mellor's , inter alia, experiments if there was considerable fluorescence in dried chlorine. This has not been shown.

The photodissociation of bromine molecules and the recombination of bromine atoms have been studied quantitatively by means of an examination of the kinetics of the hydrogen-bromine combination.

Bodenstein and Lind (31), in 1906, examined the thermal reaction $H_2 + Br_2 = 2HBr$ over the temperature range 200 - 300°C. They suggested that bromine atoms, and not the molecules, reacted with the hydrogen to form hydrogen bromide.

Later Bodenstein and Lutkemeyer (32) investigated the/

the photochemical formation of HBr at 200° C. They found that the number of bromine atoms after exposure to their source of light exceeded the number prior to illumination by some three hundredfold.

Independently, Christiansen (33), Polanyi (34), and Herzfeld (35) interpreted the experimental relations of the thermal reaction by means of the following series of reactions:-

1.	Br_2	=	Br + Br	k_1
2.	Br + H_2	=	HBr + H	k_2
3.	H + Br_2	=	HBr + Br	k_3
4.	H + HBr	=	H_2 + Br	k_4
5.	Br + Br	=	Br_2	k_5

where 1. represents the dissociation of bromine molecules owing to thermal agitation and the k's the velocity coefficients of the respective reactions.

For the photochemical reaction Bodenstein suggested that the primary action of light consisted in the dissociation of a bromine molecule into atoms, two atoms being formed for each quantum absorbed. Thus the sequence of reactions are supposed identical with those of the thermal reaction.

In the photo-stationary state, as many bromine atoms/

atoms are being formed as are recombining. Hence

$$k_1 I_{abs} = k_5 (Br)^2$$

where I_{abs} is the number of quanta absorbed, k_1 is taken as = 2, and (Br) is the concentration of bromine atoms. Bodenstein calculated the value of k_5 and found that it was about one thousand times greater than that obtained experimentally.

Shortly after this, Born and Franck (36) from a consideration of quantum mechanics, advanced the theory that for the formation of a homopolar diatomic molecule a triple collision between the two atoms and a third body is necessary. Since it can be shown that the number of ternary collisions at the pressures used is about a thousand times less than that of double ones, an explanation of Bodenstein's results is obtained.

Kondratjew and Leipunsky (37) were able to show that Born and Franck's prediction was correct. According to Born and Franck the recombination of bromine atoms takes place by the following mechanism

$$Br + Br + M = Br_2 + M.$$

Now the bromine atoms may also be lost by a reversal of the primary photochemical process viz:-

$$Br + Br = Br_2 + h\nu$$

i.e. recombination with the emission of radiation.

This/

This was the reaction examined by Kondratjew and Leipunsky at high temperatures by observing the thermo-luminescence spectra. The results showed that at moderate pressures the probability of such a reaction is practically negligible.

However, Kondratjew (38) showed later that if the pressure was about 0.7 mm., and the wavelength used was 1500 Å, then the process $Br + Br = Br_2 + h\nu$ would compete with the triple collision process.

These advancements led Jost and Jung (39) to re-examine the theory of the hydrogen bromide formation. According to their investigations the reaction velocity is inversely proportional to thesquare root of the total pressure, various inert gases being added. Thus instead of Bodenstein's relationship

$$2I_{abs} = k_5(Br)^2$$

they put

$$2I_{abs} = k_5'(Br)^2(M)$$

where (M) is the total number of molecules of any kind in unit volume and is proportional to the total pressure of the gaseous mixture.

Another interesting fact became evident from Jost's (40) work.

A consideration of the diffusion theory would lead one/

one to believe that the addition of inert gases would result in an increase of the reaction velocity by prevention of removal of atoms by the walls. This increase takes place only at low pressures of inert gas. At higher pressures the triple collision effect results in the removal of bromine atoms and hence a decrease in reaction velocity.

To account for these effects, Jost introduced another reaction to the above mechanism viz:-

$$Br + \text{wall} = \tfrac{1}{2} Br_2 + \text{wall}.$$

To allow for the change of concentration due to diffusion to the walls he introduced the term $D \frac{d^2(Br)}{dx^2}$ to the equation $2I_{abs} = k_5'(Br)^2(M)$.

(D = coefficient of diffusion
x = mean distance from centre of reaction vessel to the walls).

Thus

$$2I_{abs} - k_5'(Br)^2(M) + D \frac{d^2(Br)}{dx^2} = 0.$$

At high pressures and with a large vessel the third term may be neglected. At very low pressures and with a small reaction vessel the second term may be neglected. At intermediate pressures the expression is as stated above.

As Ritchie (41) has pointed out, Jost in his examination of the HBr formation at high pressures, did/

did not make any distinction between the relative efficiencies of the different inert gases. He merely introduced a single term $\sqrt{p_m}$. Ritchie examined the effect of foreign gases on the rate of photochemical formation of HBr at 200C. He considered the two cases (a) loss of bromine atoms by diffusion to the walls and (b) loss of bromine atoms by triple collision. In (a) i.e. at low concentrations of bromine atoms, he found that the addition of foreign gas is accompanied by an increase in the rate of reaction. The relative effects of the gases were given by

$$CCl_4 > CO_2 > \begin{matrix} N_2 \\ O_2 \end{matrix} > A > H_2 \text{ and } He.$$

In (b) i.e. at high concentrations of bromine atoms, the rate of reaction was decreased by facilitating recombination of bromine atoms. The relative collision efficiencies were given as

$$\underset{(1.00)}{CO_2} > \underset{(0.95)}{O_2} > \underset{(0.62)}{N_2} > \underset{(0.52)}{A} > \underset{(0.15)}{He} > \underset{(0.12)}{H_2}.$$

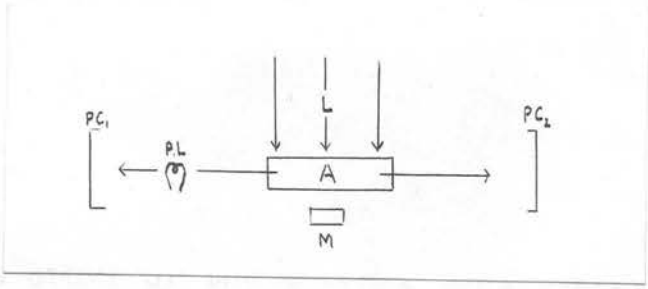
Another possibility suggested by Jost (40) for the removal of bromine atoms was the formation of an intermediate quasi-molecule (Br_2') which must be stabilised by collision or lost by dissociation within a/

a very short time after its formation. But he found that the mean life of such a molecule is of the same order of magnitude as the duration of a collision. Thus Jost concluded that the recombination of bromine atoms can only take place effectively at triple collision.

In the same paper Jost gives the results obtained for the velocity of formation of HBr when light corresponding to the band region is used. Under the same experimental conditions, he found that the velocity of formation in the band region, about 5650Å, was almost the same as in the continuum i.e. below 5107Å. It follows from this that the excited molecules resulting from absorption of light in the band region must dissociate by collision, the atoms formed being normal. The yield of atoms must be high. Jost concluded from these experiments that normal atoms are just as effective as excited atoms in the reaction.

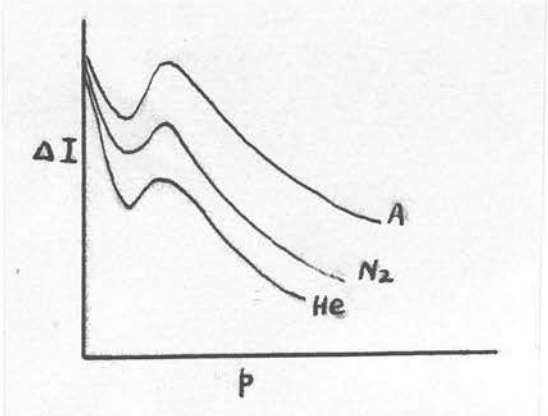
Recently Rabinowitch and Lehmann (42) in work published during the course of the present investigation, studied the photodissociation of bromine molecules and the recombination of the atoms produced/

produced by observing the decrease of the molecular absorption coefficient of the illuminated vapour. The effect of admixing inert gases was examined. Their experimental procedure was briefly as follows:-



The bromine was contained in a rectangular cell A, and was illuminated by a strong beam of light L. The change in the absorption coefficient due to dissociation was measured by means of a photoelectric compensation device consisting of a 24 watt lamp PL and two selenium-iron cells PC_1 and PC_2. The number of quanta absorbed and therefore the number of atoms produced was measured by means of a calibrated Moll thermopile-galvanometer system M.

The pressure of bromine taken was 5mm. The following types of curves were obtained by plotting ΔI (the change of absorption of light energy from PL) against the pressure of inert gas.



They explained the curves as follows:-
The addition of small quantities of inert gas causes ΔI to decrease. This they said was due to a decrease in the thermal effect (thermal dissociation) due to the higher conductivity of the gas added. The decreasing effects of the different gases are given by the following series:-

$$He > N_2 > A > CO_2 > CCl_4.$$

This is the order of the thermal conductivities of the respective gases.

Further addition of the gas causes ΔI to rise again, supposedly due to an increase in the time required for the atoms to diffuse to the walls. The pressures of the different gases required for ΔI to reach a maximum are in the order

$$He > A > N_2 > CO_2 > CCl_4,$$

which is to be expected from a consideration of the molecular diameters.

Still further additions of inert gas cause ΔI to decrease. This is due to the removal of bromine atoms by homogeneous recombination. The collision efficiency series was

$$CO_2 > N_2 > A > He,$$

which is in accordance with the series obtained by Ritchie/

Ritchie (41), Norrish (43) and others.
They also found that the homogeneous recombination was inversely proportional to the square root of the total pressure.

In an examination of the photodissociation of iodine molecules in solution Rabinowitch and Wood (44) found that the velocity of recombination of the iodine atoms in solution was about 1000 times greater than that of bromine atoms in helium at atmospheric pressure. This lends added weight to Born and Franck's hypothesis that a triple collision is necessary for homogeneous recombination. They also found that the quantum yield is the same whether absorption takes place in the band region or in the continuum.

In conclusion it is interesting to note the results recently obtained by Hilferding and Steiner (45) in an examination of the recombination of bromine atoms making use of the photochemical hydrogen bromine combination. They found that over the pressure range 258mm. to 1308mm. the relation between the velocity and the total pressure agrees with the results obtained by Jost. They were able to determine the rate of recombination of bromine atoms in triple collision with/

with various foreign molecules. They found that at high pressures the number of effective triple collisions approximates to the theoretical. Again at pressures less than 258mm. the recombination of atoms on the walls is appreciable.

PART 1.

P A R T 1.

As there has been considerable variation of opinion regarding the effect of moisture on the Budde effect, it was deemed advisable to re-investigate the problem in the particular case of bromine.

Experiment 1. In which the effect on the photo-expansion of drying bromine over pure phosphorus pentoxide was examined.

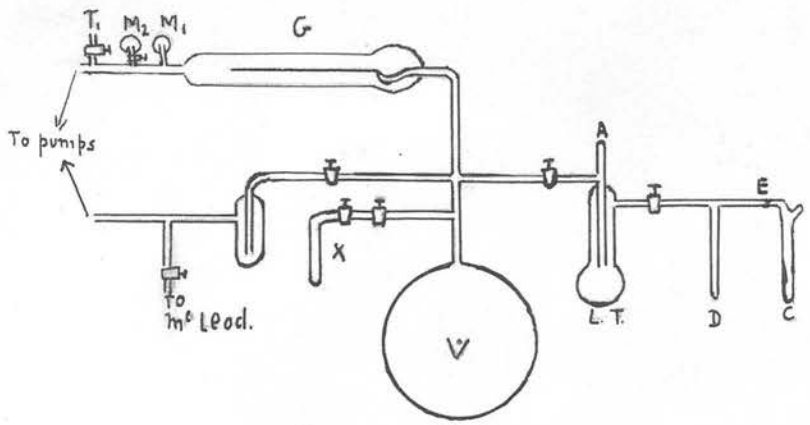


FIGURE 1

Apparatus. The apparatus for drying the bromine and measuring its photoexpansion is shown diagrammatically in Fig. 1. The insolation vessel V, spherical in shape and made of soft glass had an internal volume of 1000/

1000c.c.

The pressure gauge (G) was of the Bourdon glass-spring type and was connected to the insolation vessel as shown. The gauge pointer was observed by means of a telescope, the eyepiece of which contained a graduated scale (1 division of the scale corresponding to 0.130mm. of mercury). The gauge was used for two purposes viz:- (a) as a null instrument for measuring the total pressure of gas in the insolation vessel and (b) as a direct reading manometer calibrated against the mercury manometers for the measurement of the photoexpansion.
The gauge was used as a null instrument by (1) observing the position of the pointer image on the eyepiece scale and the level of the mercury column in the manometer M_1 (read in conjunction with the standard manometer M_2), (2) introducing bromine into the insolation vessel, (3) allowing air to enter the outer jacket of the gauge via tap T_1 until the pointer reached the original position, and (4) noting the new reading on the mercury manometer. The difference in the mercury manometer readings gave the pressure of bromine vapour taken.

Calibration of the Bourdon Gauge. The whole apparatus was/

was evacuated. The position of the gauge pointer image and the levels of the mercury columns in the manometers were observed. By introducing air into the vessel V, the pointer was deflected through several divisions, the exact number being noted. Air was now admitted to the outer jacket of the gauge which was directly connected to the manometer M_1, until the pointer image returned to the initial position. The balancing pressure of air was then read off from M_1. This process was repeated several times with different pressures of air. In this way the gauge-eyepiece scale system was calibrated and could be used directly to measure small pressure changes.

LT was a liquid air trap which had a bulb of about 100c.c. volume at the end. This bulb contained pure phosphorus pentoxide introduced via tube A.

The tap grease used was Apiezon L which has an immeasurably low vapour pressure at the ordinary temperatures. Before greasing the taps T_2, T_3, T_4, which were to be in close contact with bromine, the grease was exposed to bromine for some time. This eliminated any absorption of bromine which might take place during an experiment.

The apparatus was evacuated by means of a mercury diffusion/

diffusion pump backed by a Cenco Hyvac oil pump. With this system a pressure of 2×10^{-6} mm. of mercury (measured by a McLeod gauge) was easily obtained.

The light source was an Osram 500 watt projector lamp run at 220 volts from 230V. A.C. mains by hand controlled resistance (voltmeter across the lamp). The lamp was placed at a distance of 40cm. from the centre of the insolation vessel. Heating rays were cut out by interposing a 14cm. layer of water.

Preparation of Chemicals. Bromine bought as pure, had the last traces of chlorine removed by distilling from a solution of potassium bromide. Any traces of hydrobromic acid were removed by shaking with a very dilute solution of potassium hydroxide, separating, and finally distilling from moist zinc oxide. The bromine was kept over phosphorus pentoxide. Before using, the bromine was fractionally distilled at low pressure several times. This was done by cooling C in a mixture of carbon dioxide and acetone, and cooling the receiving tube D in liquid air. The initial and final fractions were in each case removed by pumping off. The final sample was collected in D and the constriction at E sealed off.

Phosphorus pentoxide was purified according to the method/

method suggested by Finch and Peto (46). The apparatus used is shown in Figure 2.

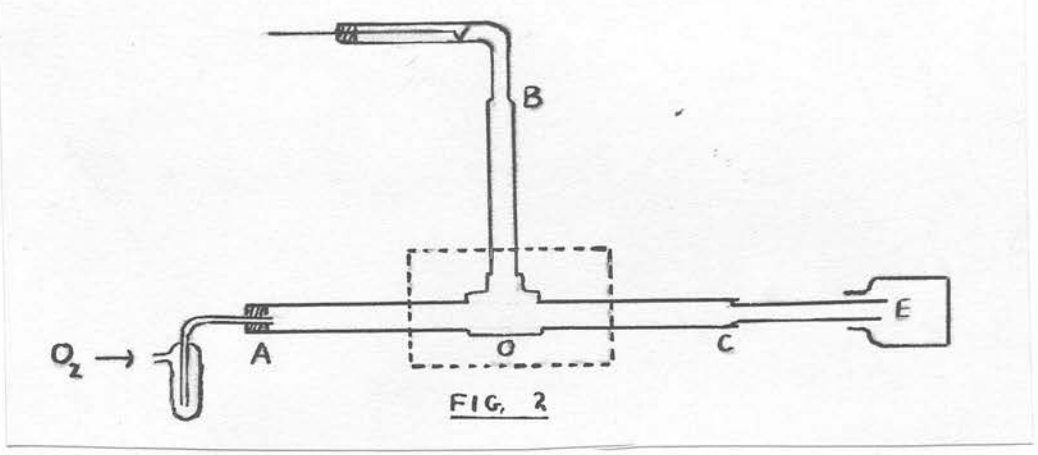


FIG. 2

OABC consisted of an inverted T-piece made of stout iron pipe. CE made of hard glass fitted fairly closely into the iron pipe. The portion enclosed by dots was heated by a series of Meker burners. Phosphorus pentoxide was dropped down tube BO sublimed in a current of oxygen (dried by passing through two traps cooled in liquid air) and collected in E. (Yield was approximately 15%). The oxide thus obtained had no reducing action on silver nitrate or mercuric chloride.

Experimental Procedure. The apparatus was evacuated and the insolation vessel " washed " out with bromine vapour. Re-evacuation was followed by introducing bromine vapour into the vessel to a pressure of 30mm. (measured by the null method described above).

Having/

Having noted the position of the gauge pointer on the eyepiece scale, the bromine was illuminated and the increase of pressure observed. The pointer moved to its maximum reading about 20 seconds after the light had been turned on and returned to its original position after the light had been switched off. This process was repeated several times, the mean value of the measured increases of pressure being recorded. Finally the bromine was pumped off.

Meanwhile liquid or solid bromine, in D, was in constant contact with phosphorus pentoxide. (The halogen was frozen out periodically on to the P_2O_5 with a carbon dioxide-acetone freezing mixture). This contact was maintained over a period of 3 months, measurement of the photoexpansion obtained with 30mm. of bromine being made once a week.

The experimental results are given in Table 1.

Results. All experiments were carried out at room temperature.

Table 1.

No. of hours dried.	(Br_2) Mm.	Increase in pressure.(mm.)
0	29.4	o.286
72	30.3	.312
288	29.7	.234
392	29.5	.260
704	29.3	.260
894	30.6	.260
1134	30.3	.260
1206	29.8	.234
1278	29.9	.234
1538	30.0	.260
2000	29.9	.260

No positive decrease in the photoexpansion of bromine on thorough drying over phosphorus pentoxide was obtained.

Experiment 2. In which the photoexpansion of dry bromine in a "baked" out vessel was examined.
The apparatus was that used in Experiment 1 with the addition of a side tube (X) with two taps to regulate the supply of water vapour.

To "bake" out, the insolation vessel was enclosed in an asbestos hot-air bath. The source of heat was a bunsen burner, the flow of gas being regulated by means of a screw-clip. A temperature of 350°C (±5°) as measured by a thermometer enclosed in the bath, was easily maintained. This temperature was considered sufficiently high to remove the adsorbed film of water from the vessel walls.

The "baking" out was done by heating to 350°C and evacuating continuously with a mercury diffusion pump backed by an oil pump for two days. At the end of this time, the bath was removed, and dry bromine was introduced into the insolation vessel to a pressure of 30mm.

The results obtained were:-

	(Br_2) mm.	Photoexpansion mm.
Prior to drying bromine and "baking" out insolation vessel.	30.0	0.260
After drying bromine and "baking" out insolation vessel.	30.0	0.260

The experiment was repeated, the same result being obtained.

The bromine was removed from the vessel V by freezing out with liquid air. Water vapour from X was admitted to V and the pressure measured by the calibrated gauge system. Bromine vapour at a pressure of 30mm. was now added and the photoexpansion observed.

The bromine-water vapour mixture was then pumped off. More water vapour was added and the process repeated.

Results.

(Br_2) = 30mm.

(H_2O) mm.	Photoexpansion mm.
0	o.260
2.1	.247
3.7	.234
6.5	.260

Thus no increase in the photoexpansion was observed on adding water vapour to dry bromine.

D I S C U S S I O N.

From the above experiments it follows that for pressures of 30mm.

(a) Thorough drying of bromine does not result in a decrease in the photoexpansion

(b) The photoexpansion of dry bromine is not decreased by the removal of the adsorbed film of water from the walls of the insolation vessel

(c) The addition of water vapour to dry bromine has no appreciable effect on the photoexpansion.

According to Franck's postulates, supported by experimental evidence, the primary process on the absorption of radiant energy corresponding to the region of continuous absorption may be represented by

$$Br_2 + h\nu = Br + Br$$

where $h\nu$ represents 1 quantum of radiant energy

(ν = frequency of radiation)
(h = constant 6.547×10^{-27} erg secs.)

At this point it seems advisable to consider the possibility of an expansion due to an increased concentration of bromine atoms.

i.e. Br_2 = Br + Br
1 vol = 1 vol + 1 vol

If the light used is of such wavelength that dissociation/

dissociation just occurs (λ = wavelength corresponding to the convergence limit viz. λ_c = 5107Å) the total energy of the bromine atoms will be equal to that of the original bromine molecule.

From the kinetic theory of gases we have

$$pv = \tfrac{1}{3}nm\bar{c}^2$$

where p = pressure
v = volume
n = number of particles
m = mass of a particle
$\bar{c}^2$ = mean square velocity.

No pressure increase or decrease will result immediately at dissociation for we can take it that the velocity of the atoms will be the same as that of the molecule. Hence $pv = \frac{1}{3}(nm\bar{c}^2)$ becomes $pv = \frac{1}{3}(2n\frac{m}{2}\bar{c}^2)$. Certainly the velocity of the atoms will increase but that of the molecules will decrease if there is to be equipartition of energy. The total energy remains the same. If the atoms get to the walls and stick or recombine there, they will remove energy from the gas and there will be a contraction.

If they recombine in the gas phase, they will give out their energy as heat and the pressure will increase.

Suppose now that the wavelength of light absorbed is less than that of the convergence limit

then/

then the excess energy may be considered as increasing the velocity of the atoms produced. Thus the pressure will increase.

A consideration of the absolute value of the energy absorbed shows that at the pressures examined only about 10^{-6} of all the molecules present are dissociated. Then if $\underset{1\ vol}{Br_2} = \underset{2vols}{2Br}$ were a fact it is easily seen that with the system of pressure measurement employed, the pressure increase due to the atomic concentration alone would not be recognisable.

When however the atoms recombine the heat given out will correspond to the energy applied by the light beam, due allowance being made for that produced by combination on the walls of the vessel. The heat produced by the latter case presumably has little or no effect in heating the main mass of the gas.

For recombination of the atoms the following mechanism (three body collision) is accepted.

$$Br + Br + M = Br_2 + M.$$

If in this equation M can only represent foreign molecules (e.g. water molecules) or the walls then it would be possible, by drying bromine, to prevent recombination of the atoms in the gas phase. All recombination would then take place on the walls the heat/

heat of recombination being transported away.

But there is no reason why a bromine molecule should not act as an efficient third body. The main criterion is that the third body must be able to take up the energy liberated by the recombination. It is generally accepted that in the case of atomic nitrogen or atomic hydrogen, the union of the atoms may take place as follows:-

$$N + N + N_2 = 2N_2$$

$$\text{and } H + H + H_2 = 2H_2.$$

In the same way therefore

$$Br + Br + Br_2 = 2Br_2.$$

If as has been suggested, an adsorbed film of water on the walls "poisons" the wall recombination then why should drying of bromine alone result in a complete disappearance of the photoexpansion? The film can only be effectively removed by prolonged "baking" of the containing vessel in vacuo. (Schwab (47) concluded that in the case of bromine atoms every collision with the walls, irrespective of the nature of the latter, resulted in combination). The wall effect probably determines the decrease in photo-expansion on drying but not in terms of the above "poisoning".

In/

In most of the previous work on the Budde effect in bromine the insolation vessels have been comparatively small. That used by Ludlam (15) had an internal volume of about 1.2c.c. while Lewis and Rideal's (17) was about 20c.c.. In such vessels and at moderate pressures the number of atoms reaching the walls will be an extremely large proportion of those produced. The presence of moisture in the bromine will impede the diffusion of atoms to the walls and may just be enough so to increase the number of homogeneous recombinations that a measurable expansion results. (Such effects will be considered in more detail in a later section).

In the present experiments the reaction vessel had a capacity of 1000c.c..

Suppose that in the different vessels mentioned above the pressure of dry bromine was the same. Consider now the equation derived by Einstein, viz.

$$x^2 = 2Dt$$

where x = linear displacement of a molecule
t = time
D = diffusion coefficient.

Consider an atom at the centre of each of the above vessels/

vessels. Let x = radius (0.6cm. 1.7cm. and 6.2cm. for the vessels mentioned). From Einstein's equation we get a measure of the time taken by the atoms in getting to the walls.

$$t_1 : t_2 : t_3 \; : : \; 0.36 : 2.9 : 38.4.$$

Thus if we let Z be the number of collisions suffered during a displacement x and if

$$Z = \frac{\bar{u}t}{l}$$

where $\bar{u}$ = root mean square velocity

l = mean free path.

Then $Z_1 : Z_2 : Z_3 \; : : \; 0.36 : 2.9 : 38.4.$

From this it is evident that in the case of the large vessel the number of atoms/[x] reaching the walls will be about 10^{-2} of those reaching the walls in the case of the small vessel. On the other hand, the introduction of a small amount of water vapour or the "poisoning" effect of an adsorbed film might reasonably be expected to have a more noticeable effect in the small vessel. As has already been mentioned in the present series of experiments, the addition of varying quantities of water vapour to 30mm. of dry bromine did not increase the photoexpansion.

It is difficult to conceive the results obtained/

[x] /assuming the same number of atoms present in each case

obtained by Narayana (25) . The pressures he was working with were 760mm. of chlorine and 250mm. of bromine. In the case of chlorine drying reduced the photoexpansion from 0.6mm. to 0.1mm., while the photoexpansion of dry chlorine in a "baked" out vessel was zero. With the bromine drying alone reduced the photoexpansion from 0.9mm. to 0.2mm.. On the basis of a paper by Hilferding and Steiner (45), the wall effect in the case of 760mm. of chlorine will be very small, and in the case of 250mm. of bromine will not be so large as to be affected by the removal of a small quantity of water vapour. In other words, at these pressures, the removal of water vapour will not greatly affect the number of homogeneous recombinations.

A possible explanation of Narayana's observations may be put forward.

It has been claimed (48) that if a mixture of hydrogen and chlorine, from which all traces of water have been removed, is exposed to visible light, no combination takes place. This has been disproved (49), the explanation of the earlier experiments being that during the drying an impurity must have been introduced/

introduced which acted as an inhibitor.

Again in experiments to be described later, it was found that the addition of small quantities of sulphur dioxide to bromine resulted in a decrease in the photoexpansion (cf. formation of sulphuryl chloride).

On this basis it seems possible that in the decreased photoexpansion observed by Narayana, the cause may have been due not so much to the removal of water vapour as to the introduction of some impurity during drying, which combined endothermically with the halogen atoms.

S U M M A R Y.

The influence of moisture on the photoexpansion of bromine has been examined.

It was found that the photoexpansion of bromine in a large vessel is not decreased by drying. The addition of water vapour to dry bromine does not give rise to an increase in the photoexpansion.

It is impossible to account for all the discordant results of previous workers owing to insufficient data as to the size of vessel, previous treatment, varying pressures etc.. We believe that the main cause of lack of agreement is that when the vessels are small, the effective surface removal of energy is greatly increased and that the presence of water vapour would retard this effect by behaving as an inert gas. The latter effect is twofold, (1) hindering the translation of the atoms to the walls, (2) increasing the recombination by triple collisions in the gas.

PART 2.

PART 2.

A. The Effect of Foreign Gases on the Photo - expansion of Bromine.

INTRODUCTION.

Within the past few years, chemical gas reactions have been subject to intense study. In consequence it has been found that in some cases, what were at one time thought to be homogeneous reactions are in reality heterogeneous. For example, surfaces have been shown to play a dominant part in reactions involving the production of atoms.

In reactions where an atom chain mechanism is postulated, it is found that the chains are broken by the recombination of the atoms. This takes place by collision in the homogeneous gas phase or at the surface of the reaction vessel or in a combination of both.

That the surface is no small disturbing factor has been shown in numerous cases by the addition of inert gases (50). If the total pressure of the reactants is low, admixture of a small amount of inert gas results in an increase in the rate of reaction./

reaction. This is interpreted as being due to the added gas impeding the movement of the atoms towards the walls of the containing vessel.

The effect of surfaces has also been studied by varying the diameter of the vessel and keeping the pressure of the reactants constant. It was found that the rates increased with the size of the vessel(51) due to the fact that the time required for chains to reach the walls is increased. Thus at low pressures the addition of an inert gas has the same effect on the velocity as increasing the diameter.

With higher pressures of inert gas it might appear that the rate of reaction should be increased still further due to the fact that the atoms taking part in the reaction will have greater difficulty in reaching the walls. What actually happens is that the rate is decreased (cf. Ritchie, Jost etc.). This has been shown as due to the removal of atoms by recombination in three body collisions.

From this it was concluded that in the determination of reaction rates, allowance must be made for the total pressure. (Inter alia, Jost (40), Semenoff (52)).

In/

In his work on the lower critical oxidation limit of phosphorus vapour, Semenoff (52) assumed that the diameters of all the molecules present were equal. He further assumed that the mean free path in the gas mixture was inversely proportional to the total pressure. Melville and Ludlam (53) claimed that a more specific factor must be introduced and showed in their experiments that the chain lengths depended not only on the concentrations of the gases present but also on their respective diffusion coefficients.

According to the Stephan-Maxwell theory for the diffusion of a binary mixture,

$$D \propto \frac{1}{(x)\,\sigma_{AX}^{2}\left(\frac{1}{M_A}+\frac{1}{M_X}\right)^{-\frac{1}{2}}}$$

Where D = the diffusion coefficient

M_A = molecular weight of the particle diffusing

M_X = molecular weight of inert gas

(x) = pressure of inert gas

σ_{AX} = sum of radii of gas molecule and diffusing particle.

Consider now a single molecule diffusing through a mixture of three gases. Let the diffusion coefficients/

coefficients of each gas separately be D_1, D_2, and D_3. If t is the time required to diffuse a given distance then it may be assumed that

$$t \propto \left(\frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3} \right).$$

According to Ritchie (41) in an examination of the effects of inert gases on the photosynthesis of hydrogen bromide, if S represents the rate at which bromine atoms get to the walls and are removed, then S is inversely proportional to t

$$\text{i.e.} \quad S \propto \left(\frac{1}{D_1} + \frac{1}{D_2} + \frac{1}{D_3} \right)^{-1} .$$

With these facts in hand the effects of pressure and of "foreign" gases on the photoexpansion of bromine were examined as will be shown in the following description of the series of experiments.

Description of the Experimental Method.

Apparatus. The apparatus used is shown diagrammatically in Fig. 3.

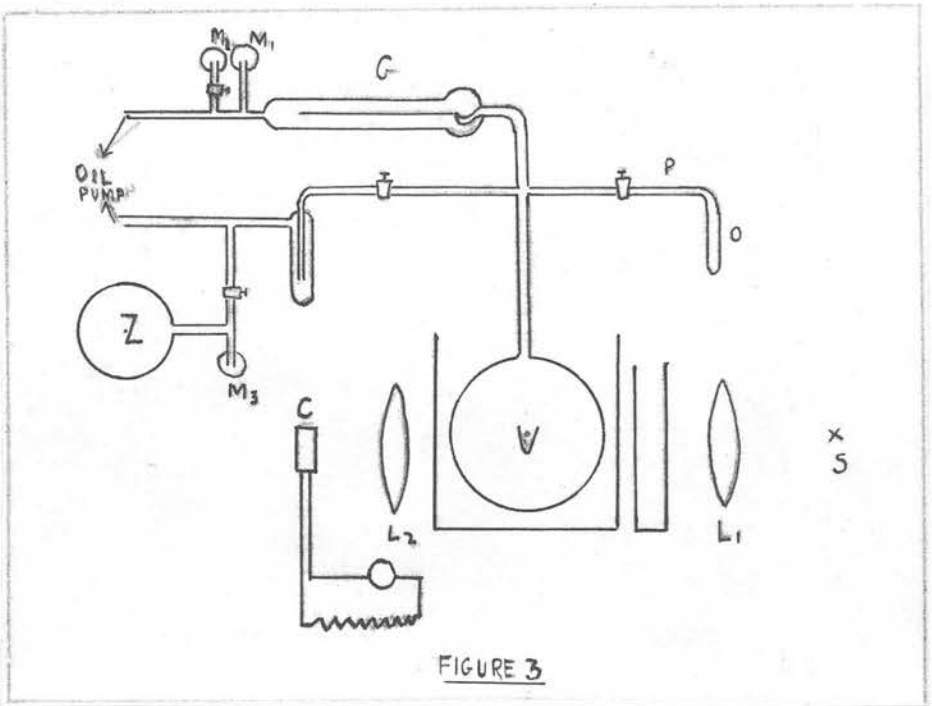


FIGURE 3

The spherical insolation vessel V, made of soft glass, had an internal volume of 1500c.c. and was connected to the Bourdon gauge as shown. The vessel was immersed in water, contained in a bath which had plane glass walls. (The temperature of the water was that of the room which did not vary by more than ± 1°C in the course of a day).

The gauge G was used as described in Part 1. (1 division of eyepiece scale ≡ 0.210mm. mercury). O was the bromine reservoir. Z was a reservoir for inert/

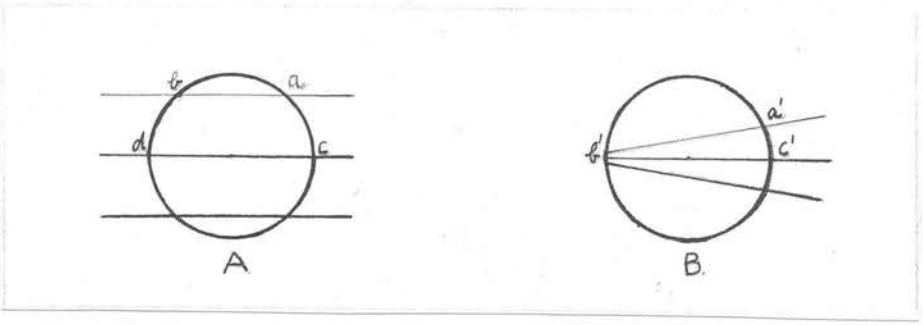
inert gases, M_3 being a mercury manometer used to give an indication of the amount of gas in Z.

P was a tube about 4cm. diameter, loosely filled with pure phosphorus pentoxide. This was used to ensure that the moisture content of the bromine was at a minimum.

The light source S was a 500 watt projector lamp. As shown by a voltmeter, the lamp was run at 220 volts from a 230 volts A.C. mains by hand controlled resistance. By means of a condenser lens L_1, a convergent beam of light was made to fall upon the insolation vessel. Since the latter was spherical a convergent beam seemed preferable to a parallel beam. The reasons for this were:-

(a) To obtain parallel light meant reducing the intensity of the incident beam. (b) The loss of light by reflection at the surface would be greater in the case of a parallel beam. (c) With such an insolation vessel the path-length of every "particle" of radiant energy would be approximately the same if the incident beam were convergent.

(This may be easily seen from the following:-



In case A the beam of light is parallel. The path-length cd is considerably greater than ab. In case B where the light is convergent the path-lengths c'b' and a'b' are comparable).

Before entering the vessel, the light was passed through a 14cm. layer of a 2% solution of copper sulphate.

The emerging beam of light was focussed on to a Weston Photronic cell C, by means of a condenser lens L_2. The cell, shielded from external radiations, was connected in series with a Weston galvanometer and a fixed resistance. This system always gave perfectly reproducible results.

The apparatus was readily evacuated to a pressure of less than 0.01mm. by means of a Cenco Hyvac oil pump.

Preparation of Materials. Bromine and phosphorus pentoxide were purified as described in Part 1.

Before collecting in the reservoir, argon (99.5%), nitrogen (99%), oxygen (97%), carbon dioxide all supplied/

supplied in cylinders by the British Oxygen Company, sulphur dioxide (from a siphon) and air were bubbled slowly (2 bubbles per second) through two wash bottles containing concentrated sulphuric acid and then passed through a tube about 20cm. long loosely packed with phosphorus pentoxide. Before use, argon, nitrogen, oxygen and air were passed through a liquid-air trap.

Experimental Procedure. The apparatus was evacuated. The transmitted light intensity I_o at zero pressure of bromine was then measured by means of the Photronic cell system. The levels of the mercury columns in the manometers and the initial position of the gauge pointer image were observed. After "washing" out with bromine vapour, bromine was introduced into the insolation vessel by way of tap T_1 to the desired pressure. The light was switched on, adjusting the voltage to 220 volts, and the deflections of the gauge pointer and galvanometer needle observed. In this way the photoexpansion and transmitted light intensity I at the pressure (Br_2) were measured. This process was repeated several times no positive deviations being observed.

In examining the effect of "foreign" gases, the pressures of bromine used were in general 30, 40, and 50mm./

50mm.. Having recorded the photoexpansion and the light energy absorbed ($I_{abs} = I_o - I$) for the particular pressure, the "foreign" gas was added to the required pressure followed by redetermination of the transmitted light intensity and measurement of the photoexpansion. Before observing the photo-expansion, the bromine-gas mixture was allowed 15 minutes for complete mixing; this was found to be necessary as otherwise incorrect results were obtained.

THEORETICAL DISCUSSION Of The EXPERIMENT.

The bromine atoms produced by the absorption of light may be considered in two divisions -

(a) those recombining in the gas phase by triple collision, the heat of combination appearing in the gas phase and causing an increase of pressure,

(b) those removed by surface action.

Thus when bromine is subjected to the action of light of wavelength corresponding to the region of continuous absorption the above effects may be represented by the following scheme.

No.	Reaction.	Velocity Coefficient.
1.	$Br_2 + h\nu = Br + Br$	k_1
2.	$Br + Br + M = Br_2^{\times} + M^{\times}$	k_M
3.	$Br + wall = \frac{1}{2} Br_2$	S

where coefficient S depends on the velocity of diffusion of bromine atoms through the gas mixture. The heat of combination of bromine atoms on the walls does not appear to any appreciable extent in the gas phase as an increase in pressure since it is removed by the thermostat.

If the vessel is large and the pressure high recombination according to mechanism No. 2 will be predominant/

predominant. The total heat appearing in the gas phase will be equivalent to the energy absorbed (Iabs) and will be independent of the gases present (except in so far as Iabs alters with the addition of foreign gases). The temperature rise however depends on the nature of the gas mixture as well as on the rate of cooling i.e. the Budde effect depends on the gas, while the heat does not. This is only the case when (2) is predominant.

In the photostationary state we see from the above mechanism that

$$\frac{dBr}{dt} = k_1 Iabs - k_M (Br)^2(M) - S(Br) = 0.$$

Suppose now that the rise in temperature, i.e. the increase in pressure Δp, is due entirely to heat produced in the gas and that heat produced on the surface does not affect Δp.

Then

$$\text{heat produced} \propto k_M (Br)^2(M).$$

In the steady state, the rise in temperature of the system will further depend on the thermal conductivity of the gas mixture. The heat transferred to the walls per second will be equal to the heat produced per second.

Now if we consider two horizontal planes, one at/

at a temperature T_1, the other at a lower temperature T_0, separated by a distance x, then the quantity of heat Q transferred across an area A is approximately given by

$$Q = \frac{KA(T_1 - T_0)}{x}$$

where K is the thermal conductivity. If A and x are constant we have

$$Q \propto (\Delta T)K.$$

Let us return to the case of a gas. When the pressure of a gas is sufficiently high (see later experiments) the thermal conductivity is independent of the pressure.

Now in the present experiments with a relatively narrow beam traversing the gas mixture and with walls at a fixed temperature (thermostated)

$$Q \propto (\Delta T)K$$

where T represents the rise in temperature. But the increase in pressure is proportional to the rise in temperature

$$\therefore Q \propto \Delta pK.$$

On this basis

$$K \Delta p \propto k_M(Br)^2(M)$$

or $$RK \Delta p = k_M(Br)^2(M)$$

where R is a constant.

Since/

Since

$$k_M (Br)^2 (M) + S (Br) - k_1 Iabs = 0$$

the concentration of bromine atoms in the steady state can be determined.

Thus

$$(Br) = \frac{-S \pm \sqrt{S^2 + 4k_1 Iabs(k_M)M}}{2Mk_M}$$

k_1 may be taken as 2 and since (Br) must be positive

$$(Br) = \frac{-S + \sqrt{S^2 + 8I_{abs}k_M M}}{2Mk_M}$$

But

$$RK\,\Delta p = k_M M(Br)^2 = 2I_{abs} - S(Br).$$

Hence on substituting for (Br)

$$RK\,\Delta p = 2I_{abs} - \frac{S}{2Mk_M}\left[\sqrt{S^2 + 8I_{abs}k_M M} - S\right] \quad \ldots\ldots(1)$$

As we have already seen, if t is the time taken for a bromine atom to diffuse a given distance through bromine

$$t \propto \frac{1}{D_{Br_2}}$$

where D_{Br_2} represents the diffusion coefficient for a bromine atom through bromine

and $$S \propto \frac{1}{t} \propto D_{Br_2}$$

where/

Where $D \propto \frac{1}{(Br_2)\sigma^2_{Br-Br_2}} \left(\frac{1}{M_{Br}} + \frac{1}{M_{Br_2}} \right)^{\frac{1}{2}}$

Therefore $S_{Br_2} = \frac{m}{(Br_2)\sigma^2_{Br-Br_2}} \left(\frac{1}{M_{Br}} + \frac{1}{M_{Br_2}} \right)^{\frac{1}{2}}$

where m is a constant dependent on, among other things, the vessel dimensions.

<u>The Effect of adding Foreign Gases.</u> In considering Equation 1 for bromine-inert gas mixtures, Mk_M must be replaced by

$$\left[(Br_2)k_{Br_2} + (X)k_X\right]$$

where (X) is the pressure of inert gas.

Thus Equation 1 becomes

$$RK\,\Delta p = 2I_{abs} - \frac{S}{2\left[(Br_2)k_{Br_2} + (X)k_X\right]}\left[\sqrt{S^2 + 8I_{abs}\left[(Br_2)k_{Br_2} + (X)k_X\right]} - S\right] \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

or say

$$RK\,\Delta p = 2I_{abs} - Y,$$

whence $$I_{abs} = \frac{1}{2}(RK\,\Delta p + Y) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

K, the thermal conductivity will naturally differ for each individual gas mixture. For all practical purposes, the thermal conductivity may be taken as varying/

varying linearly with the gas composition (cf. the thermal conductivity of oxygen-hydrogen mixtures given in the International Critical Tables Vol.5 p. 214). The values given for K (loc. cit. p.213) are

Gas	$K \times 10^5$
A	1.58
N_2	2.28
O_2	2.33
CO_2	1.37
Air	2.23

The values calculated from $K = \cdot f\eta C_V$ where η is the viscosity, C_V the specific heat at constant volume and f is a constant (for monatomic gases 2.5, diatomic 1.75, triatomic 1.4) were approximately 2.5 times those given in the Critical Tables. The value of K calculated for bromine was 1.1×10^{-5}. To bring this value into line with those given above we get $\frac{1.1}{2.5} \times 10^{-5} = 0.44 \times 10^{-5}$.

RESULTS.

Examination of Equation 2. shows that at high pressures and with a large reaction vessel the value of the S factor becomes small. In other words, under these conditions $\frac{2I_{abs}}{\Delta p}$ tends to a constant value. Hence from the curve obtained by plotting $\frac{2I_{abs}}{\Delta p}$ against the total pressure, we can, by extrapolation, determine the value of R approximately. At zero pressure of inert gas, the R term becomes small and the value of m in the S factor important. Therefore taking $k_{Br_2} = 1.0$ we can determine the value of m. The values of R and m having been thus determined, the intermediate pressures give the value of k_X.

m will depend largely on the concentration of bromine atoms produced and will therefore vary slightly for the different series examined viz. 30, 40 and 50mm. of bromine.

The constants used in the calculations were:-

$K_{Br_2} = 0.44$, $K_A = 1.58$, $K_{N_2} = 2.28$, $K_{O_2} = 2.33$, $K_{Air} = 2.23$.

$k_{Br_2} = 1.0$, $k_A = 0.5$, $k_{N_2} = 0.8$, $k_{O_2} = 0.9$.

The following values were taken for the molecular radii/

radii:-

$\sigma_{Br} = 1.0\times10^{-8}$cm., $\sigma_{Br_2} = 1.7\times10^{-8}$cm., $\sigma_{A} = 1.43\times10^{-8}$cm.,

$\sigma_{N_2} = 1.55\times10^{-8}$cm., $\sigma_{O_2} = 1.45\times10^{-8}$cm.

The ratio of the value of the right hand side to the left hand side of Equation 3. is given in the final column of each Table.

Inert Gas Effect of Nitrogen.

TABLE 1.

(Br_2) = 50mm., R = 24.0, m = 5.0×10^{-11}.

(N_2) mm.	Δp mm	I_{abs} div.	$\frac{2I}{\Delta p}$	RKΔp	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{RHS}{LHS}$
0.0	0.336	21.7	129.0	3.54	41.1	22.3	1.02
64.2	.357	21.9	122.7	12.54	33.8	23.17	1.05
136.4	.420	22.0	104.7	17.95	25.4	21.7	0.99
170.7	.483	22.1	91.3	21.20	21.9	21.55	0.98
235.0	.567	22.2	78.3	26.70	17.45	22.1	1.00
284.6	.609	22.3	73.2	29.22	14.75	21.98	0.99
336.5	.651	22.3	68.4	31.90	12.5	22.2	1.00
390.6	.672	22.4	66.7	34.50	10.7	22.6	1.01
441.7	.714	22.4	62.8	35.90	9.4	22.6	1.01
494.1	.735	22.5	61.2	38.80	8.77	23.1	1.02
567.4	.777	22.5	58.0	39.80	8.0	22.9	1.02

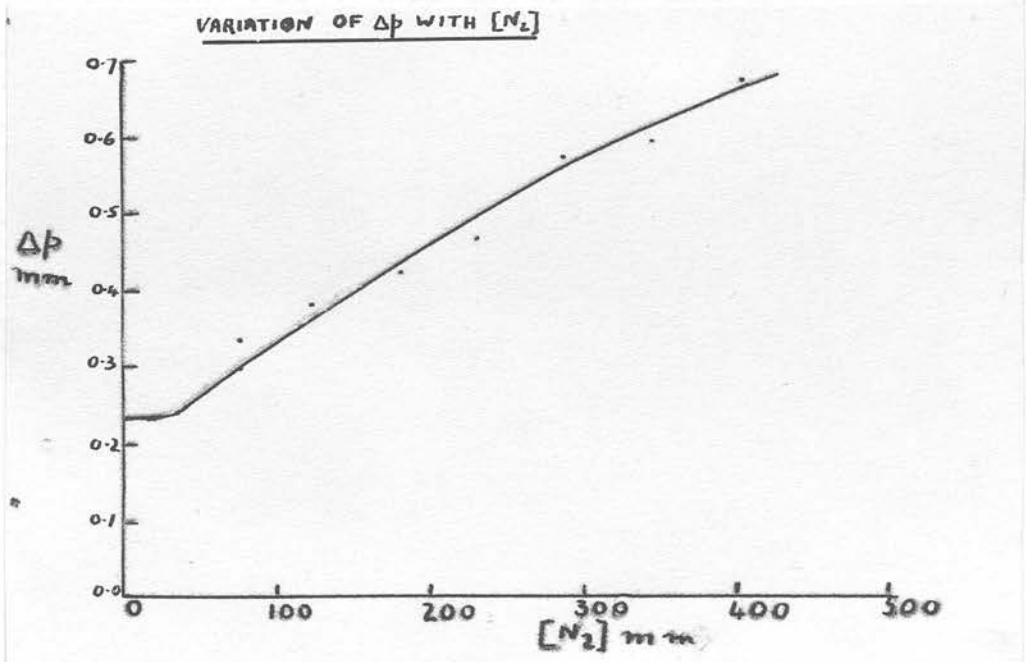


FIGURE 4.

TABLE 2.

(Br_2) = 40mm., R = 24.0, m = 3.5×10^{-11}.

(N_2) mm.	Δp mm	I_{abs} div.	$\frac{2 I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p + Y)$	$\frac{R.H.S.}{L.H.S.}$
0.0	0.273	19.9	146	2.88	37.6	20.24	1.02
15.4	.273	19.9	146	6.25	36.1	21.17	1.06
41.0	.294	20.0	136	9.67	32.9	21.28	1.06
72.7	.336	20.1	119	12.90	29.7	21.3	1.06
132.9	.378	20.5	108	16.10	22.2	19.15	0.93
187.4	.462	20.5	89	21.70	17.3	19.5	0.95
240.0	.504	20.6	82	24.30	13.1	18.7	0.92
292.0	.567	20.9	73.6	27.80	12.1	19.95	0.97
348.2	.630	20.9	66.2	31.70	9.7	20.7	0.99
424.7	.714	20.9	58.7	36.20	7.8	22.0	1.05

TABLE 3.

(Br_2) = 30mm., R = 19.0, m = 5.0×10^{-11}.

(N_2) mm	Δp mm	I_{abs} div.	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p + Y)$	$\frac{R.H.S}{L.H.S.}$
0.0	0.231	17.9	155	1.9	35.1	18.5	1.03
12.1	.231	18.0	156	4.3	35.0	19.6	1.09
24.3	.231	18.2	158	5.5	34.9	20.2	1.11
54.6	.273	18.5	136	8.4	33.3	20.9	1.13
75.5	.336	18.5	110	11.2	31.6	21.4	1.16
124.6	.378	18.9	100	13.8	26.9	20.3	1.07
182.6	.420	19.0	91.0	16.35	21.7	19.0	1.00
232.0	.462	19.1	83.0	18.15	18.1	18.1	0.95
289.0	.567	19.1	67.4	22.75	15.7	19.2	1.01
346.2	.588	19.2	65.3	23.85	12.3	18.1	0.94
406.0	.672	19.2	57.2	27.4	10.3	18.9	0.98
480.0	.777	19.2	49.5	32.0	8.4	20.2	1.05

Inert Gas Effect of Argon.

TABLE 4.

(Br_2) = 50mm., R = 24.0, m = 5.0×10^{-11}.

(A) mm	Δp m.m	I_{abs} div.	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{R.H.S.}{L.H.S.}$
0.0	0.336	21.6	129	3.54	40.6	22.07	1.02
20.0	.357	21.7	122	6.57	39.7	23.13	1.06
40.1	.378	21.7	115	8.69	37.0	22.84	1.05
60.0	.420	21.8	104	10.7	35.6	23.1	1.06
80.0	.441	21.9	99.7	12.2	33.8	23.0	1.05
128.0	.546	22.0	80.9	16.5	28.6	22.55	1.02
178.7	.609	22.0	73.0	19.4	23.6	21.5	0.98
243.6	.735	22.0	60.0	24.5	18.95	21.73	0.99
294.8	.798	22.1	55.4	27.2	16.25	21.73	0.99
351.8	.840	22.2	53.0	28.9	13.8	21.35	0.97
424.8	.945	22.4	47.5	33.1	11.4	22.25	0.99
485.0	1.02	22.4	44.1	36.0	9.95	22.98	1.02

TABLE 5.

(Br_2) = 40mm., R = 24.0, m = 3.5×10^{-11}.

(A) mm.	Δp mm.	I_{abs} div.	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{R.H.S.}{L.H.S.}$
0.0	0.273	19.9	146	2.88	37.6	20.24	1.02
10.6	.294	20.0	136	4.78	36.3	20.54	1.03
24.7	.315	20.0	127	6.60	35.5	21.05	1.05
39.0	.357	20.1	113	8.55	33.8	21.2	1.05
60.2	.420	20.1	95.6	11.35	31.2	21.3	1.06
72.9	.441	20.2	91.6	12.3	30.0	21.15	1.04
101.4	.483	20.3	84.1	14.6	26.5	20.55	1.02
151.8	.567	20.3	71.8	17.6	24.6	21.1	1.04
204.0	.630	20.6	65.4	21.05	17.2	19.1	0.93
253.4	.756	20.8	55.1	25.7	17.45	20.1	0.96
302.1	.819	20.9	51.2	28.5	12.13	20.3	0.97
354.2	.882	21.0	47.6	30.7	10.4	20.55	0.98
401.6	.945	21.0	44.5	33.6	9.05	21.3	1.01
538.5	1.05	21.0	40.0	37.8	6.34	22.1	1.05

TABLE 6.

(Br_2) = 30mm., R = 19.0, m = 5.0×10^{-11}.

(A) mm	Δp mm.	$I_{abs.}$ div.	$\frac{2 I_{abs.}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p + Y)$	$\frac{R.H.S.}{L.H.S}$
0.0	0.231	17.9	155	1.90	35.1	18.5	1.03
13.8	.252	18.0	143	3.80	35.05	19.4	1.08
25.7	.273	18.2	133	5.00	35.0	20.0	1.10
50.6	.315	18.5	118	6.90	34.4	20.6	1.11
70.5	.336	18.7	111	7.90	33.6	20.7	1.11
119.3	.441	18.9	86.0	11.3	30.2	20.7	1.09
169.2	.504	19.0	75.2	13.5	26.1	19.8	1.04
228.6	.672	19.0	56.5	18.5	21.6	20.0	1.05
276.0	.693	19.0	55.0	19.4	18.8	19.1	1.00
341.3	.735	19.1	52.0	20.7	15.6	18.2	0.95
388.5	.840	19.3	46.0	23.8	13.8	18.8	0.98
454.0	.987	19.3	39.2	28.4	11.7	20.0	1.04
576.0	1.09	19.3	38.0	31.4	9.0	20.2	1.05

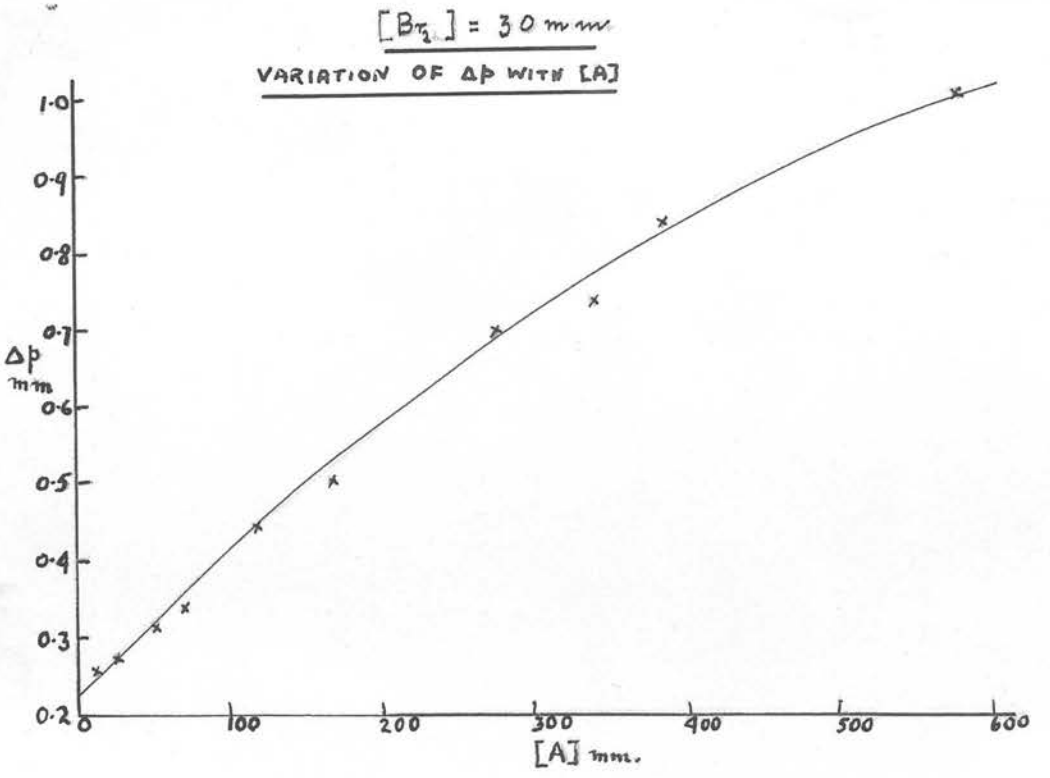


FIGURE 5.

Inert Gas Effect of Oxygen.

TABLE 7.

(Br_2) = 40mm., R = 24.0, m = 3.5×10^{-11}.

(O_2) mm	Δp mm	I_{abs} div.	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{R.H.S}{L.H.S.}$
0.0	0.273	19.5	143	2.88	37.3	20.1	1.03
21.0	.231	19.6	-	-	-	-	-
41.0	.231	19.8	-	-	-	-	-
62.0	.231	19.9	-	-	-	-	-
79.9	.315	20.0	127	12.8	27.0	19.9	1.00
100.0	.336	20.0	119	14.4	25.0	19.7	0.98
149.9	.378	20.1	106	17.5	18.8	18.15	0.90
202.5	.441	20.2	91.8	21.3	15.0	18.15	0.90
253.1	.504	20.2	80.2	25.2	12.2	18.7	0.93
301.0	.567	20.2	71.5	28.7	10.1	19.4	0.97
352.0	.630	20.3	64.5	32.4	8.57	20.5	1.01
400.0	.672	20.3	60.5	34.9	7.54	21.2	1.04

TABLE 8.

(Br_2) = 30mm., R = 19.0, m = 5.0×10^{-11}.

(O_2) mm.	Δp mm.	I_{abs} div.	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{R.H.S}{L.H.S.}$
0.0	0.231	17.9	155	1.90	35.1	18.5	1.03
7.7	.231	17.9	155	3.63	34.5	19.1	1.06
16.8	.210	18.0	171	4.46	34.25	19.35	1.08
26.3	.231	18.1	157	5.80	33.8	19.8	1.10
36.2	.231	18.2	158	6.30	33.2	19.75	1.09
62.4	.252	18.3	145	8.20	32.2	20.2	1.11
79.0	.315	18.4	117	10.8	30.9	20.85	1.14
99.0	.357	18.4	103	12.8	28.6	20.7	1.12
121.1	.378	18.5	98.0	14.1	26.8	20.45	1.11
140.3	.399	18.5	92.9	15.1	24.75	19.93	1.08
186.7	.420	18.7	89.2	16.5	20.0	18.25	0.98
334.3	.609	18.9	62.2	25.2	12.4	18.8	0.99
387.3	.693	19.0	54.9	29.0	10.6	19.8	1.04
457.8	.714	19.0	53.2	30.0	8.73	19.36	1.02

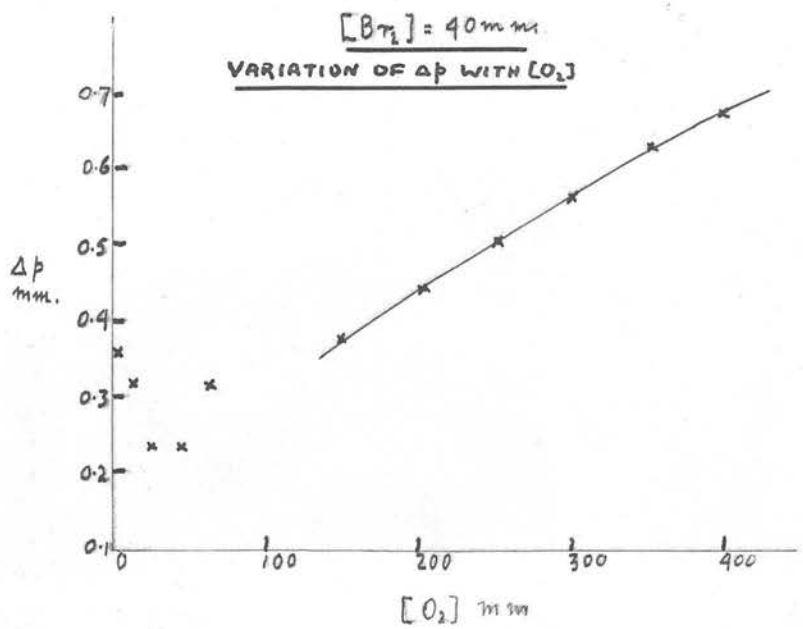

[Br2] = 40 mm
VARIATION OF Δp WITH [O2]
Δp mm.
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1/100
1/200
1/300
1/400
[O2] m m

FIGURE 6

Inert Gas Effect of Air.

TABLE 9.

(Br_2) = 50mm., R = 24.0, m = 5.0×10^{-11}.

= 1.53×10^{-8} cm., $'k'_{Air}$ = 0.85.

(Air) mm.	Δp mm.	I_{abs} div	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{R.H.S}{L.H.S}$
0.0	0.336	21.7	129	3.54	41.1	22.3	1.03
25.3	.336	21.8	130	8.48	39.8	24.14	1.10
75.6	.336	22.0	141	11.9	35.75	23.8	1.08
124.7	.377	22.2	118	15.5	31.4	23.45	1.06
174.3	.441	22.3	101	19.3	25.5	22.4	1.00
232.8	.483	22.5	93.4	22.1	21.0	21.55	0.96
289.5	.546	22.6	83.0	25.8	17.45	21.63	0.96
351.1	.609	22.6	74.4	29.2	14.6	21.9	0.97
413.0	.630	22.6	72.0	30.8	11.7	21.25	0.94
472.9	.777	22.6	58.3	38.3	10.7	24.5	1.08
525.3	.799	22.6	56.8	39.5	10.15	24.8	1.10

TABLE 10.

(Br_2) = 40mm.R = 24.0, m = 3.5×10^{-11}.

(Air) mm	Δp mm	I_{abs} div.	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	$\frac{R.H.S.}{L.H.S.}$
0.0	0.273	19.9	145	2.88	37.6	20.24	1.02
64.5	.294	20.1	137	10.9	30.7	20.8	1.04
99.9	.357	20.2	113	14.7	26.8	20.75	1.03
139.0	.378	20.4	108	16.6	22.6	19.6	0.96
176.4	.420	20.7	98.2	19.2	19.4	19.3	0.93
215.5	.482	20.9	87.0	22.6	16.8	19.7	0.94
273.2	.525	20.9	79.9	25.4	13.54	19.5	0.93
330.5	.587	20.9	71.3	28.8	11.24	20.0	0.96
393.3	.630	20.9	66.6	31.2	9.40	20.3	0.98
459.3	.672	21.0	62.6	33.6	7.89	20.75	0.99

In Tables 9 and 10 the values were calculated taking $k_{Air} = 0.85$, $\sigma_{Air} = 1.53\times10^{-8}$ cm, and $M_{Air}=14.5$. k_{Air} is just a convenient symbol. Strictly speaking air should be treated as a mixture (approximately 75.5% nitrogen, 23.3% oxygen and 1.2% argon etc.).

On this basis the bromine-air mixture of Table 11 is treated as Br_2 - N_2 - O_2 (neglecting argon, etc.) in their appropriate proportions with the correct ~~and~~ molecular weights. Then

$$S \propto \left(\frac{1}{D_{Br_2}} + \frac{1}{D_{N_2}} + \frac{1}{D_{O_2}}\right)^{-1}$$

and $k_M M$ becomes $\left[(Br_2) + k_{N_2}(N_2) + k_{O_2}(O_2)\right]$

TABLE 11.

(Br_2) = 30mm., R = 19.0, m = 5.0×10^{-11}

(Air) mm	Δp mm	I_{abs} air	$\frac{2I_{abs}}{\Delta p}$	$RK\Delta p$	Y	$\frac{1}{2}(RK\Delta p+Y)$	R.H.S. / L.H.S.
0.0	0.231	17.9	155	1.9	35.1	18.5	1.03
28.8	.231	18.1	157	5.8	35.1	20.45	1.12
44.9	.231	18.4	160	6.63	34.4	20.5	1.14
63.8	.273	18.5	136	8.61	32.3	20.45	1.11
90.9	.315	18.5	118	10.7	30.1	20.4	1.10
129.8	.357	18.7	103	12.86	26.4	19.6	1.05
164.8	.399	18.8	94.4	14.8	23.1	19.0	1.01
215.9	.420	18.9	90.1	16.0	19.2	17.6	0.93
252.0	.483	18.9	78.5	18.7	17.3	18.0	0.95
296.0	.546	19.0	69.6	21.5	14.5	18.0	0.95
375.0	.630	19.1	60.6	25.1	11.3	18.2	0.95
511.9	.735	19.2	52.2	29.8	8.5	19.1	1.00

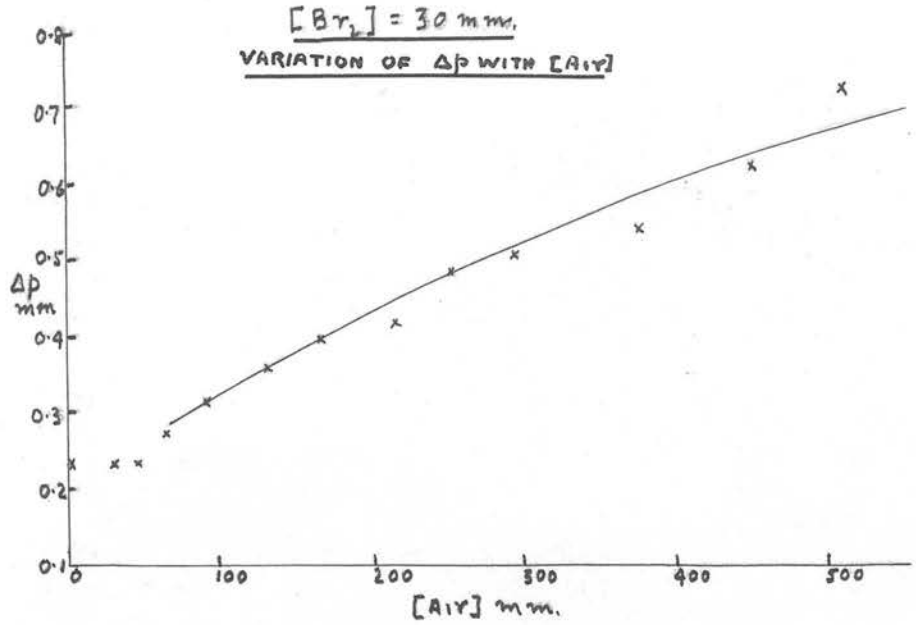


FIGURE 7

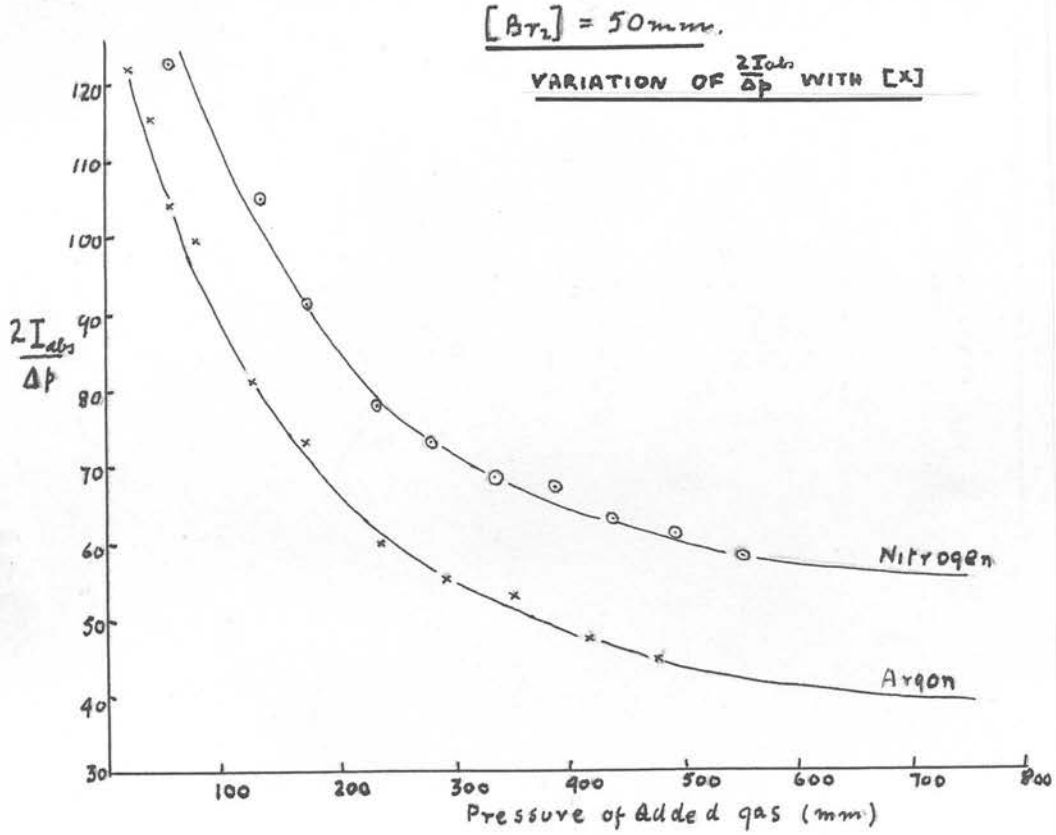


FIGURE 8

Inert Gas Effect of Carbon Dioxide.

TABLE 12.

(Br_2) = 30mm.

(CO_2) mm	I_{abs} div	Δp mm
0.0	17.9	0.231
6.3	18.1	.231
13.7	18.5	.231
22.8	18.6	.252
35.9	18.7	.273
49.0	18.9	.294
96.0	19.0	.336
167.8	19.4	.420
247.6	19.5	.504
317.6	19.7	.588
318.1	19.8	.693
377.9	19.8	.714
419.9	19.8	.756
477.8	19.8	.798
527.9	19.9	.840

TABLE 13.

(Br_2) = 40mm.

(CO_2) mm	I_{abs} div.	Δp mm.
0.0	20.0	0.273
6.3	20.0	.273
14.4	20.0	.273
28.1	20.0	.294
44.0	20.1	.336
73.6	20.4	.315
123.4	20.6	.399
173.7	20.8	.399
222.3	20.8	.504
275.2	20.9	.567
327.6	21.0	.609
370.3	21.0	.672
424.0	21.1	.714
467.3	21.1	.777
513.4	21.1	.798

TABLE 14.

(Br_2) = 50mm.

(CO2) mm.	I_{abs} div.	Δp mm.
0.0	21.6	0.357
11.2	21.6	.357
59.8	22.0	.357
113.1	22.0	.399
158.4	22.1	.462
207.9	22.2	.504
276.2	22.5	.588
337.0	22.6	.630
375.6	22.6	.672

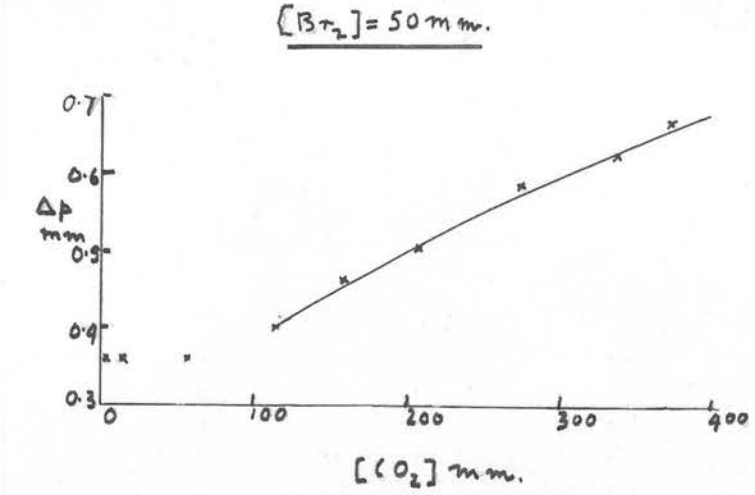


FIGURE 9.

Inert Gas Effect of Sulphur Dioxide.

TABLE 15.

(Br_2) = 30mm.

(SO_2) mm	I_{abs} div.	Δp mm
0.0	17.8	0.232
7.5	17.9	.168
14.3	18.0	.168
25.0	18.1	.147
33.8	18.3	.189
44.0	18.3	.210
55.9	18.4	.232
59.1	18.7	.232
81.8	18.8	.232
95.0	18.8	.273
138.4	18.8	.336
179.9	18.9	.378
223.9	18.9	.441

TABLE 16.

(Br_2) = 40mm.

(SO_2) mm.	I_{abs} div.	Δp mm.
0.0	20.0	0.273
7.1	20.1	.231
14.2	20.1	.210
20.9	20.2	.231
28.4	20.6	.252
37.2	20.7	.231
47.5	20.7	.252
59.9	20.8	.252
71.8	20.8	.294
84.7	20.9	.294
118.8	21.1	.315
158.7	21.1	.378
201.2	21.1	.441
249.3	21.3	.483
292.6	21.4	.525
336.8	21.5	.567
426.3	21.5	.651

TABLE 17.

(Br_2) = 50mm.

(SO_2) mm.	I_{abs} div.	Δp mm.
0.0	21.7	0.336
8.7	21.9	.294
22.5	22.2	.252
33.7	22.2	.252
44.7	22.3	.273
59.9	22.4	.294
87.6	22.5	.357
115.2	22.5	.378
156.6	22.6	.420
196.5	22.6	.441
245.5	22.7	.483
302.3	22.7	.567
360.8	22.7	.714
399.8	22.8	.735
442.9	22.8	.777

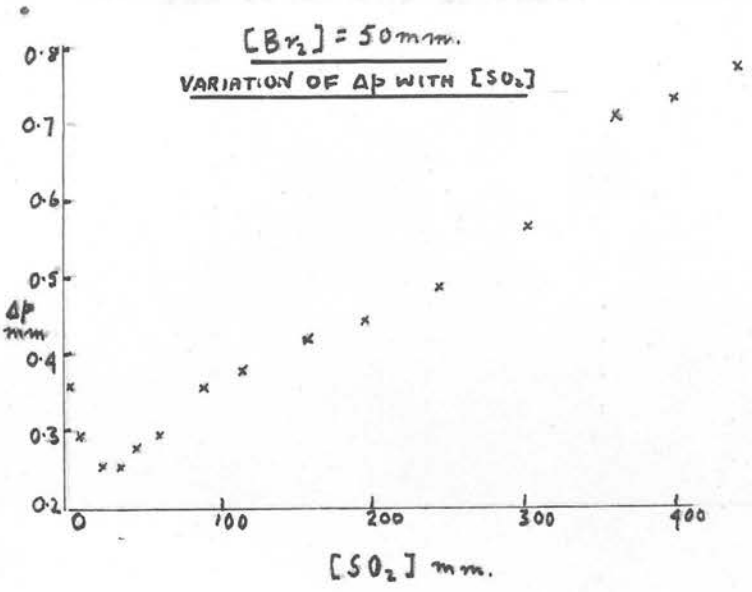


FIGURE 10

The Variation of the Photoexpansion and Energy Absorbed with the Pressure of Bromine.

With the apparatus described above (p.46) the variation of the photoexpansion and energy absorbed with the pressure of bromine was examined. Table 18 is typical of the results obtained. The experimental procedure described on page 49 et seq. was employed. The values in the column headed RK were obtained from the relationship established above viz:-

$$RK\Delta p = 2I_{abs.} - Y$$

In the calculation of the value of S, m is taken to be 5.0×10^{-11} $\sigma_{Br} = 1.0\times10^{-8}$ cm. and $\sigma_{Br_2} = 1.7\times10^{-8}$ cm. k_{Br_2} is taken as unity.

TABLE 18.

(No inert gas present).

(Br_2) mm.	Δp mm.	I_{abs} divs.	$2I_{abs}/\Delta p$	RK
7.3	0.084	8.8	210	
12.9	.105	12.2	232	
21.4	.168	15.8	188	0.47
26.9	.210	17.3	165	0.53
31.9	.231	18.5	160	0.94
36.8	.252	19.7	156	4.76
43.9	.294	20.5	139	5.96
47.1	.315	21.2	135	6.68
53.6	.378	21.9	116	7.40
59.9	.399	22.7	114	10.4
68.3	.420	23.3	111	14.8
72.7	.441	23.8	108	16.2
77.9	.462	24.1	104	17.8
95.5	.504	25.3	100	26.8

The variation of the photoexpansion with the pressure of bromine is shown in Fig. II

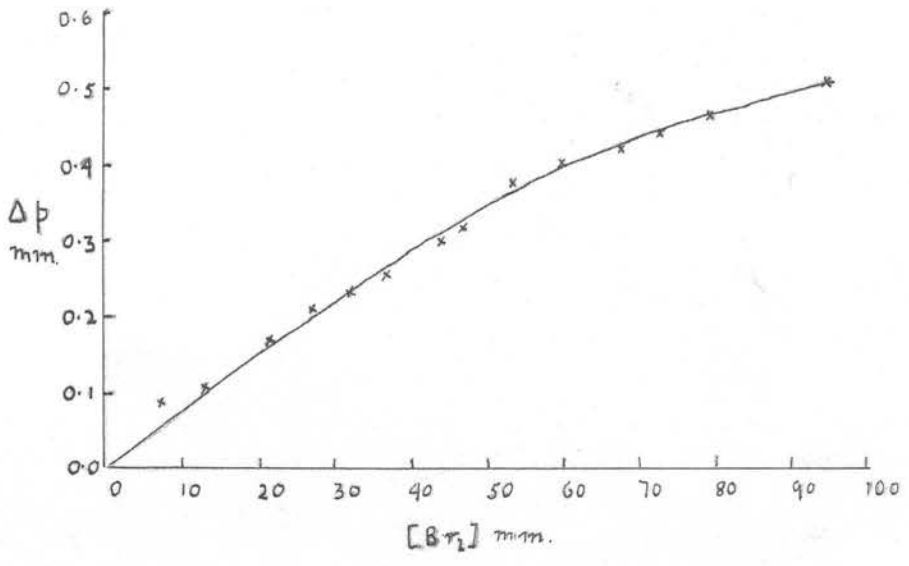


FIGURE. II

Fig.12 shows the variation of I_{abs} with the pressure of bromine (Br_2).

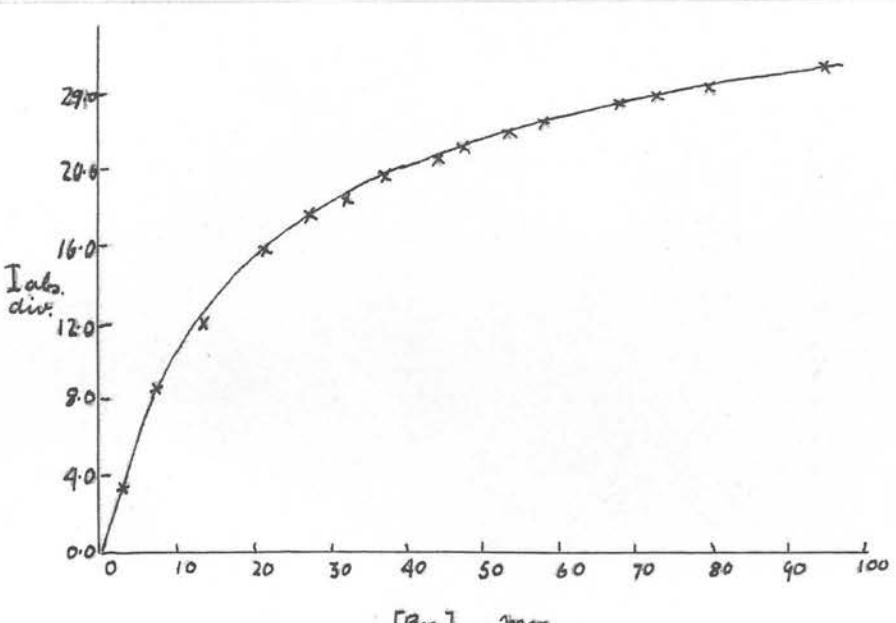
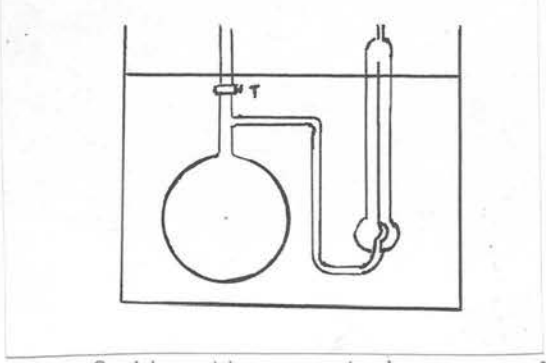


FIGURE 12

Since the curves shown above, where (Br_2) is plotted against I_{abs} and Δp had not quite reached their maxima, it was deemed advisable to examine the variations with higher pressures of bromine.
The apparatus used was somewhat similar to that shown in Diagram 2.

In this case however the Bourdon gauge (1 division eyepiece scale = 0.095mm.) was partly submerged in a thermostat as shown in the following diagram.



The temperature of the thermostat was maintained at 25°C. At this temperature pressures of bromine up to 200mm. could be used with safety (vapour pressure of bromine at 25°C = 214mm. vide. Inter. Crit. Tables). The tap T connecting the insolation vessel to the bromine reservoir was kept under water. Bromine vapour was admitted to the vessel by steaming the connecting tubing. After admission tap T was closed.

The source of light was a 500 watt projector lamp. The beam was filtered through a 6cm. layer of a 10% solution of cupric chloride. All other details were essentially the same as in the previous experiment.

TABLE 19.

$[B_{T_2}]$ mm	Δp mm	I_{abs} div.	$\frac{2 I_{abs}}{\Delta p}$
10.2	0.114	13.2	232
20.0	.218	19.5	178
31.0	.255	22.9	180
41.4	.313	24.9	160
52.5	.360	25.1	139
63.0	.408	27.0	132
82.0	.455	28.1	123
104.1	.475	29.0	122
125.0	.550	29.4	107
147.0	.570	29.6	104
167.2	.580	29.9	103
198.5	.616	30.0	99.5

The curves obtained were:-

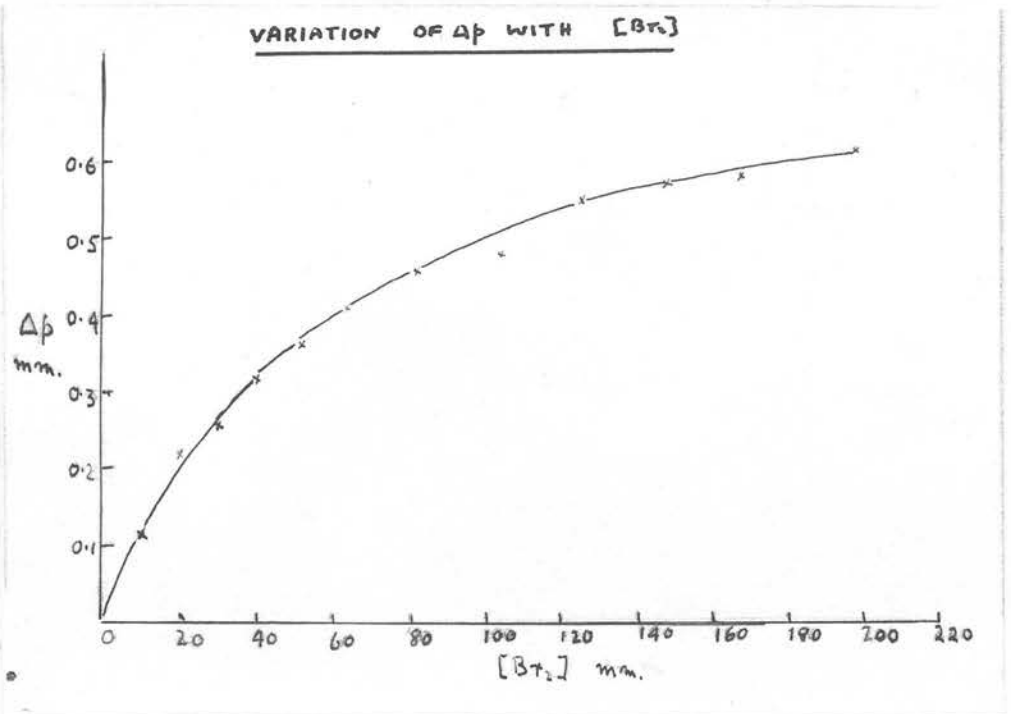


FIGURE 13

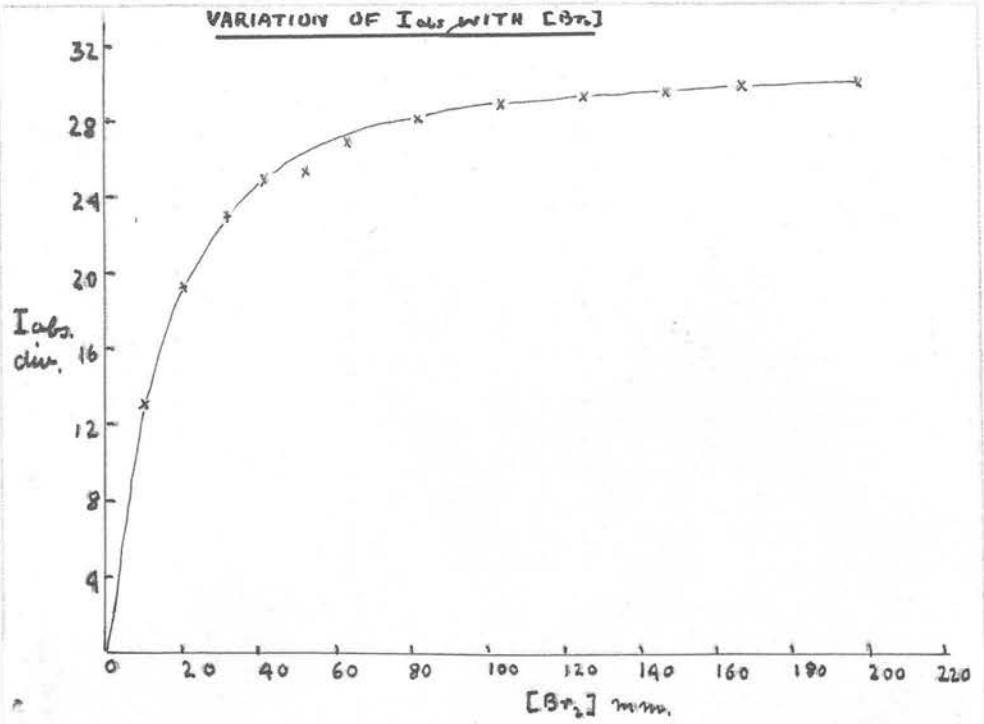


FIGURE 14

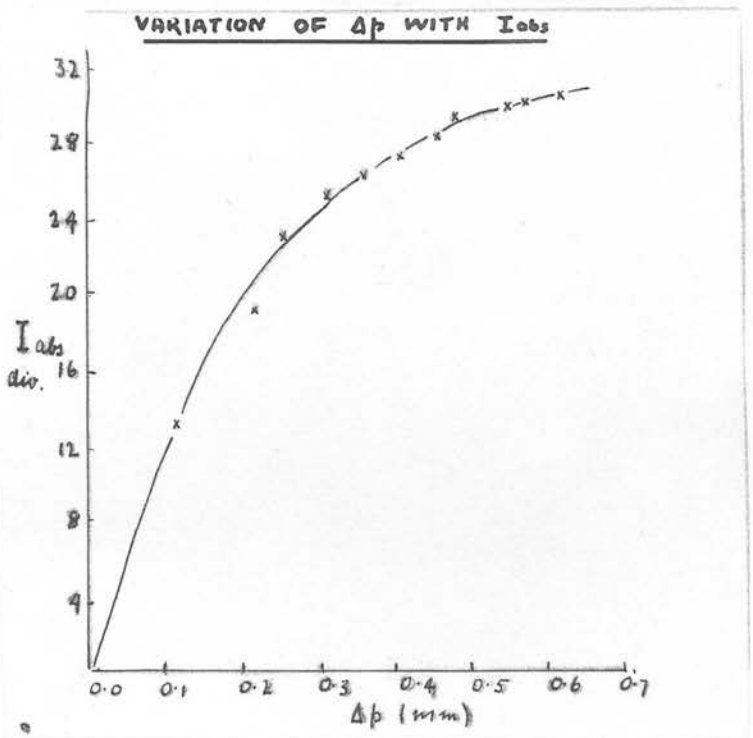


FIGURE 15

Note on the Effect of Pressure on the Thermal Conductivity of Bromine.

Equation 1 is based on the assumption that the thermal conductivity of a gas is independent of the pressure. This is not strictly the case, although Maxwell from a consideration of the kinetic theory of gases predicted that there should be no variation over a wide range of pressures. This depends on the fact that halving the number of molecules by halving the pressure allows the molecules to travel twice as far.

However if the pressure is lowered so that the mean free path of the molecules becomes comparable with the size of the vessel, the thermal conductivity will decrease.

To demonstrate this point we might quote the results obtained by Senftleben and Riechemeir (54) which show that at low pressures, thermal conductivity is a function of the pressure.

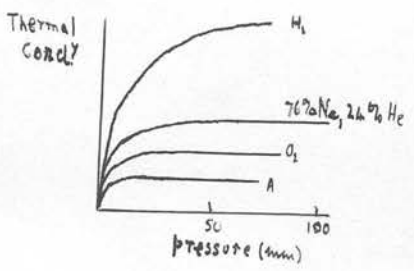


FIGURE 16

Fig. 16 shows that with a light gas such as hydrogen the/

the thermal conductivity has not reached a steady value even at a pressure of 100mm. With argon the thermal conductivity becomes constant when the pressure is about 10mm. From this it would appear that the thermal conductivity of bromine should become independent of the pressure when this is considerably less than 10mm.

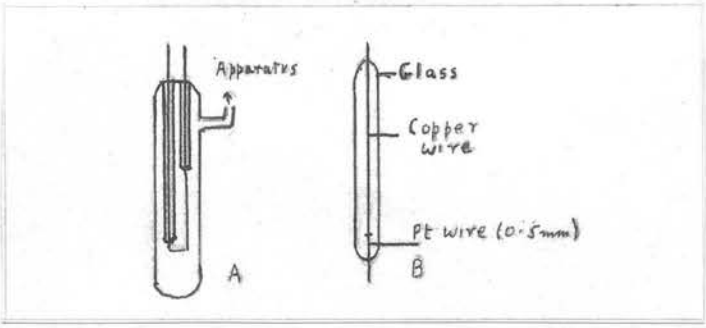
On thisbasis the variation of the thermal conductivity of bromine with pressure was examined. The experiments performed depended on the fact that when a hot wire is suspended in a gas-containing vessel the walls of which are at a lower temperature than the wire, heat flows from the wire to the walls. Increase in the conductance causes an increase in the heat flow. This cools the wire and therefore lowers its resistance.

(Senftleben and Germer (55) have shown that platinum wire may be used with bromine without fear of chemical interaction).

EXPERIMENT.

The apparatus used was the same as shown in Diagram 1 except that the vessel V was replaced by a tube 20cm. × 3cm. This was kept in an electrically heated thermostat maintained at 25°C (± 0.01°C). A platinum wire 0.015mm. diameter and 7cm. long was suspended/

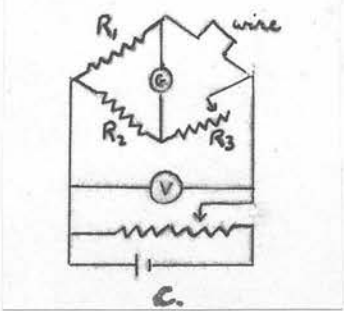
suspended in the tube as shown in Diagram A.



The leads, "pinch-sealed" into the tube, consisted of borated copper wire encased in glass capillaries (see Diagram B.). The copper wire was "spot-welded" to platinum wire (0.5mm. diameter) which in turn was welded to the gauge wire.

Before making any experimental measurements the gauge wire was glowed for some time in bromine vapour.

The method adopted was to keep the applied voltage constant and measure the change in resistance as the pressure was varied. The circuit used is shown in Diagram C.



R_1 and R_2 are fixed resistances. R_3 is varied to keep the bridge balanced. G is a suspension type galvanometer (resistance = 103.3 ohms, deflection per micro-ampere/

micro-ampere at 1 metre = 330mm.). V is a voltmeter. The voltage across the bridge is varied by means of the potentiometer arrangement shown.

PROCEDURE.

The apparatus was evacuated. The voltage applied to the circuit was about 0.8 volt. R_2 and R_3 were set at 5000 ohms. R_1 was varied until the bridge was almost balanced. Balance was obtained by a slight variation of R_3. After this R_1 and R_2 were not touched. Bromine, the pressure of which was measured by means of the calibrated Bourdon gauge system, was then admitted to the tube. The resistance of the wire decreased. R_3 was altered until the bridge was balanced. The change of resistance with varying pressures of bromine was thus observed.

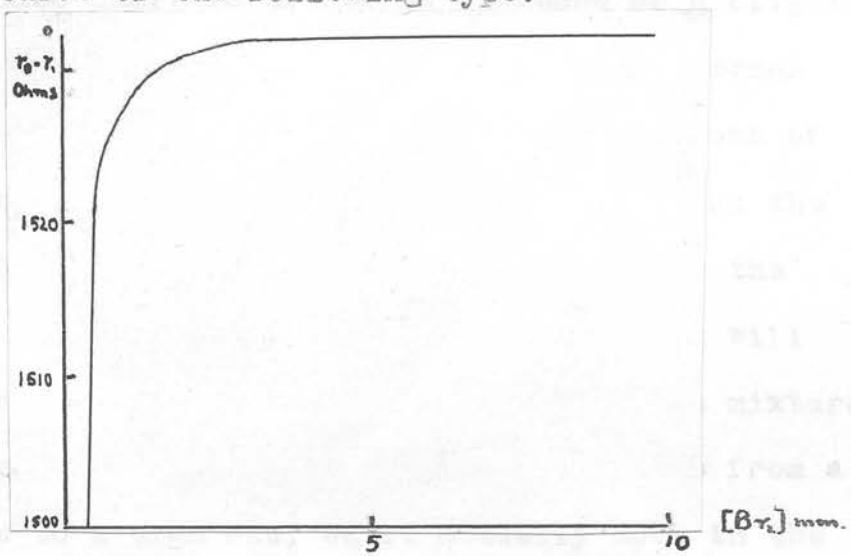
The value of R_3 before and after admission of bromine is given by r_o and r_1. The change of resistance of the wire will be proportional to $r_o - r_1$.

The results obtained are given in Table 20 overleaf.

TABLE 20.

(Br2) mm	r_o Ohms	r_1 Ohms	$r_o - r_1$ Ohms
0.357	5128	3621	1507
0.63		3605	1523
2.36		3598	1530
2.78		3596	1532
4.35		3594	1534
5.92		3596	1532
9.24		3604	1524
11.60		3601	1527
14.21		3598	1530
17.19		3596	1532
20.39		3596	1532
26.49		3597	1531
33.30		3597	1531
39.40		3596	1532
45.80		3596	1532
51.80		3597	1531
61.30		3596	1532

Plotting $(r_o - r_1)$ against the pressure of bromine gives a curve of the following type:-



This shows that the thermal conductivity of bromine reaches a constant value when the pressure is somewhere between 2 and 3 mm. Hence with the pressures used in the examination of the photoexpansion of bromine it is safe to say that K is constant.

DISCUSSION Of The RESULTS.

From the results it is obvious that the magnitude of the photoexpansion of bromine, within the range of pressure in which it can be directly measured, is intimately connected with the light energy absorbed, the thermal conductivity and the total pressure. (By thermal conductivity we mean, the rate at which the energy escapes to the walls. Convection which would be negligibly small with the light employed is ignored).

Let us consider the various facts separately. The curves (FIGS. 4-7) obtained by plotting Δp, the expansion, against the pressure of inert gas show that at the lower pressures of gas added there is either no increase or a slight decrease in Δp. This is to be expected on thermal conductivity grounds alone. The first additions of inert gas will produce no appreciable effect on the number of bromine atoms recombining. However the observed increase of pressure on illumination will depend on the thermal conductivity of the gas mixture. If this changes rapidly in the initial stages from a low value to a high one, as it actually does in the case of, say, nitrogen, then Δp will be smaller relatively and may well fall below the original

$(N_2) = 0$ /

$(N_2) = 0$ value. This phenomenon is more noticeable with nitrogen and oxygen than with argon. The thermal conductivity of the latter is considerably lower than that of nitrogen and oxygen. Again the decrease in Δp will be more noticeable with the lower pressures of bromine (e.g. 30mm.), since the increase in thermal conductivity on adding inert gases will increase more rapidly than in the case where the pressure is already high (e.g. 50mm.).

Further addition of inert gas causes K to tend to a constant value viz. that of the thermal conductivity of the inert gas alone. However the time required for the atoms to diffuse to the walls is increased as is also the number of homogeneous triple collisions. The latter effects outweigh the former and an increase in the photoexpansion is observed.

The effect on the rate of diffusion to the walls and on the homogeneous recombinations of increasing the pressure is readily seen from the fact that the value of Y (in the above Tables) steadily decreases. At very high pressures the value of Y should become zero. (The experiments show that even at pressures between 500mm. and 600mm. the wall effect has not entirely disappeared).

At/

At high pressures of inert gas K and I_{abs} are roughly constant and S becomes small. Hence Equation 2 becomes

$$RK\Delta p = 2I_{abs} - \frac{S\sqrt{8I_{abs}\left[(Br_2)k_{Br_2} + (X)k_X\right]}}{2\left[(Br_2)k_{Br_2} + (X)k_X\right]}$$

$$= 2I_{abs} - \frac{S\sqrt{2}\sqrt{I_{abs}}}{\sqrt{(X)k_X}}$$

$(Br_2)k_{Br_2}$ is small compared with $(X)k_X$

But $S \propto \frac{1}{X}$

Therefore plotting Δp against $\frac{1}{X\sqrt{X}}$ should give a straight line.

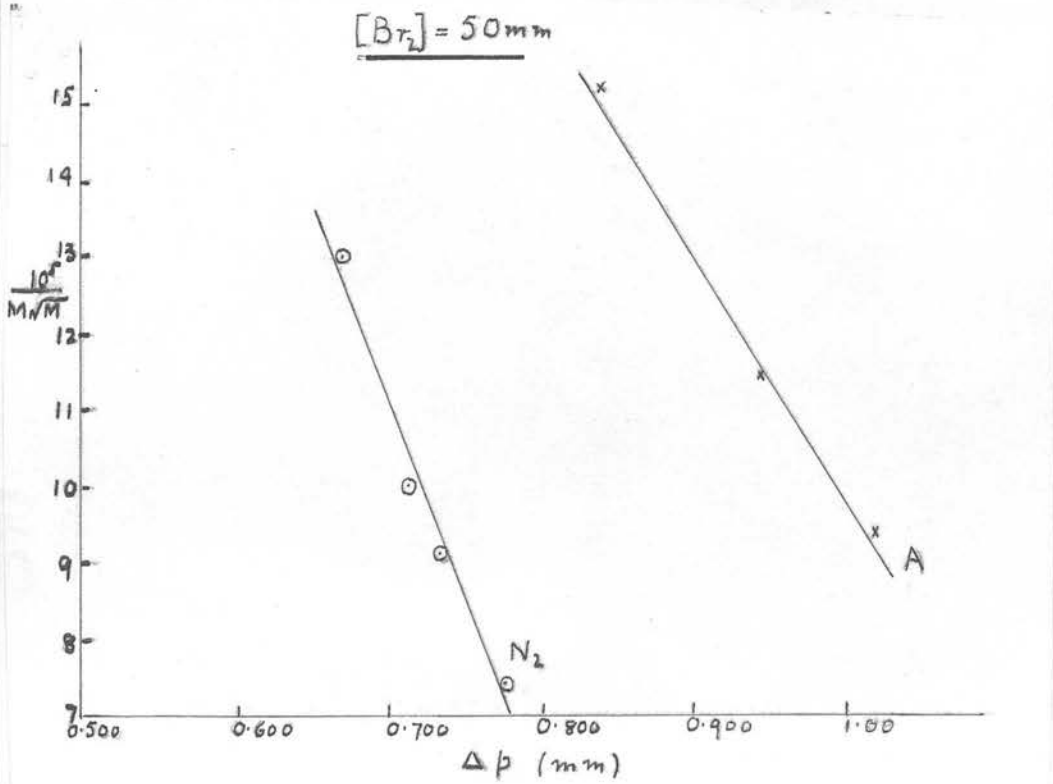


FIGURE 17

At very high pressures of inert gas

$$RK\Delta p = 2I_{abs}$$

i.e. $\frac{2I_{abs}}{\Delta p}$ tends to a constant value viz. RK.

This is shown in Fig. (8).

Thus at high pressures of added gas the limit value of $\frac{2I_{abs}}{\Delta p}$ should be given in each case by RK where K represents the thermal conductivity of the mixture. Neglecting the relatively small pressure of bromine present the ratio of the limit values of $\frac{2I_{abs}}{\Delta p}$ for nitrogen and argon is $\frac{55}{38} = 1.5$ whereas the ratio of the respective thermal conductivities $= \frac{2.28}{1.58} = 1.45$, which is in satisfactory agreement.

For some reason or other the results obtained with carbon dioxide do not come into line with the others. Impossible values for k_{CO_2} are obtained.

The results with sulphur dioxide are similar. The decrease in the value of Δp on the initial additions is greater than would be expected on a purely thermal conductivity basis[1] (Fig. 10). The thermal conductivity of sulphur dioxide is 0.768×10^{-5}. This is low compared with the value of K for argon. Yet the decrease in the/

the photoexpansion is very noticeable even though the increase in the thermal conductivity on adding sulphur dioxide is not so rapid. It might appear that the cause of this decrease is removal of bromine atoms by some chemical reaction. (Cf. $SO_2 + Br_2 = SO_2Br_2$).

We have seen that the addition of a truly inert gas increases the photoexpansion by facilitating the homogeneous recombination. The relative efficiencies of the triple collision processes is given by

$$Br_2 > O_2 > Air > N_2 > A$$

where the determined collision efficiencies are

$k_{Br_2} = 1.0$, $k_{O_2} = 0.9$, "k"$_{Air} = 0.85$, $k_{N_2} = 0.8$, $k_A = 0.5$.

Taking $k_{N_2} = 1$, the series obtained may be compared with the series obtained in other reactions.

Reactions	HCl	Cl_2	Br_2	CO_2	O_2	N_2	A	Ne	He	H_2
Br+Br (room temp)			1.25		1.13	1.00	0.62			
Br+Br(1) (200 C)				1.38	1.38	1.00	0.64		0.41	0.51
Cl+NCl_3(2)		2.24		2.24	1.47	1.00	0.94		0.55	0.55
H+O_2(3)	(5.35)	(3.47)		2.2	1.17	1.00	0.59	0.29	0.24	1.33
O+O_2(4)					0.90	1.00	0.63			
Br+Br(5)	6.3		4.8			1.00	0.12		0.31	0.5

(1) Ritchie, Proc. Roy. Soc., A 146, 828, (1934).
(2) Griffiths and Norrish, Trans. Far. Soc., 27, 451, (1931). Proc. Roy. Soc., 135, 69, (1932).
(3) Ritchie, unpublished results.
(4) Ritchie, Proc. Roy. Soc., A 146, 848, (1934).
(5) Hilferding and Steiner, Z. Phys. Chem., B30, 399, (1935).

Similarly, as we have already seen, Rabinowitch and Lehmann (42) found that the collision efficiency series in the recombination of bromine atoms is given by

$$CO_2 \rangle N_2 \rangle A \rangle He.$$

From the above it seems probable that the relative efficiencies of any two gases, say nitrogen and argon, in a stabilising triple collision will be approximately the same no matter what that triple collision is. In the same way, it is possible that the relative series are independent of temperature (Cf. first two series above) and hence the energy of activation of the process is probably zero, in agreement with the usual ideas regarding the frequency of the stabilising process. It is to be noted that while the $e^{-E/RT}$ is thus unity, the collision factor Z varies considerably: the ratio of extreme values above is roughly 20.

Until more accurate values of collision efficiencies are obtainable and until the various contradictory results have been explained, it is not reasonable to examine in detail the mechanism of the removal of energy in the stabilising triple collision. It does appear however that two factors are predominant (1) the molecular weight of the third molecule, (2) the number of degrees of freedom of the third molecule.

Thus/

Thus in the monatomic gases the collision efficiency series is given by

Kr > A > Ne > He

but N_2 > A in spite of the decreased molecular weight.

In the experiments with pure bromine it appears (see Figs. 13 and 14) that when absorption of light is complete, the photoexpansion still tends to increase. Under such conditions further addition of bromine does not result in an increase in the production of bromine atoms but increases the number of homogeneous recombinations. In other words bromine now acts as an inert gas.

As in the inert gas experiments $\frac{2I_{abs}}{\Delta p}$ tends to a constant value.

It will be observed that the value of RK in Table 18 is not constant. No single value of m can be expected to cover the whole range of bromine pressures. This is due to the fact that both the light absorption and the rate of escape of the atoms to the walls alter as a result. Only when the pressure of bromine is constant in a series can a constant value of m be employed in that series.

In Tables 1 to 17 it is seen that the value of I_{abs} increases on the addition of inert gas. This effect has/

has been observed by Weigert and Kellermann (56) with a mixture of hydrogen and chlorine, by Jost (40) and by Ritchie (41) with a mixture of hydrogen, bromine and various inert gases. It is interesting to note that Burgess and Chapman (57) did not detect any difference in the light absorption by pure chlorine or its mixture with air or hydrogen. Similarly Koehler (58) found that argon does not alter the absorption of iodine.

This increase in absorption has been considered akin to the broadening of the discrete absorption bands by the added gas molecules. The broadening of the absorption bands of bromine has been observed by Ribaud (59). He examined the spectra of bromine, bromine in air at atmospheric pressure and bromine in hydrogen at a pressure of one atmosphere. With the bromine-air mixture there was decided broadening of the bands and this was very great with the bromine-hydrogen mixture.

It has been claimed by Dhar and Bhargava (60) in a semi-quantitative paper on chemical reactivity and light absorption by a molecule/is associated with a that increased absorption weakening of the binding forces. This weakening, they say, will take place when one reacting substance is in contact/

contact with another. In the case of a hydrogen - bromine mixture they maintain that the hydrogen sensitises the dissociation of bromine molecules and makes them reactive in radiations of longer wavelengths than normal.

It appears, that if broadening of the bands is the reason for the increase in the absorption coefficient on adding inert gases, then this is due to perturbation of the molecular forces and less exact quantisation of the energy, absorption taking place over a narrow range of frequencies instead of at a single definite frequency.

S U M M A R Y.

Investigation has been made of the photoexpansion of bromine. An equation has been developed, in which the relationship between the photoexpansion, the thermal conductivity, the total pressure and the light energy absorbed is shown.

The effect on the photoexpansion of bromine of adding various foreign gases has been examined. The addition of such gases, in general, increases the photoexpansion by facilitating the homogeneous recombination of bromine atoms. The series representing the efficiencies of the triple collision process is given by

$$O_2 \rangle \text{ Air} \rangle N_2 \rangle A.$$

A comparison has been made between the relative efficiencies of triple collision processes in different reactions.

The variation of the photoexpansion and of the thermal conductivity with the pressure of bromine has been examined.

In conclusion I heartily thank Dr. E.B. Ludlam, under whose supervision the work was carried out, for the advice and encouragement which he so freely gave, and also Professor Kendall for having afforded me the opportunity to carry out this work. My thanks are also due to the Trustees of the Earl of Moray Fund for a grant towards the cost of apparatus.

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